

# Extraction of Aluminum and Iron from Bauxite: A Unique Closed-Loop Ore Refining Process Utilizing Oxalate Chemistry

Ankit Verma<sup>1</sup>, David Corbin<sup>1</sup>, and Mark Shiflett<sup>1</sup>

<sup>1</sup>University of Kansas School of Engineering

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## Abstract

The Bayer process holds an exclusive status for alumina extraction, but a massive amount of caustic “red mud” waste is generated. In this work, three oxalate reagents: potassium hydrogen oxalate ( $\text{KHC}_2\text{O}_4$ ), potassium tetraoxalate ( $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ), and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) were investigated for the Al and Fe extraction process from NIST SRM 600 – Australian Darling range bauxite ore. More than 90% of Al and Fe was extracted into the aqueous phase in less than 2 h with 0.50 M  $\text{C}_2\text{O}_4^{2-}$  for all three reagents. The Fe and Al can be selectively precipitated by hydrolyzing the aqueous phase. By acidifying the Al and Fe free filtrate, 80% of the  $\text{C}_2\text{O}_4^{2-}$  can be precipitated as  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . Greater than 90% of the aqueous acid can also be recycled using a cation exchange resin. The proposed closed-loop process is an energy-efficient, cost-effective, environmentally-friendly route for extracting Al and Fe from bauxite ore.

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Ankit Verma<sup>a,b</sup>, David R. Corbin<sup>b</sup> and Mark B. Shiflett<sup>a,b\*</sup>

<sup>a</sup>Institute for Sustainable Engineering, University of Kansas, 1536 W. 15<sup>th</sup> St., Lawrence, KS 66045, USA

<sup>b</sup>Chemical and Petroleum Engineering, University of Kansas, 1530 W. 15<sup>th</sup> St., Lawrence, KS 66045, USA

\*Corresponding Author. Email: Mark.B.Shiflett@ku.edu

## ABSTRACT

The Bayer process holds an exclusive status for alumina extraction, but a massive amount of caustic “red mud” waste is generated. In this work, three oxalate reagents: potassium hydrogen oxalate ( $\text{KHC}_2\text{O}_4$ ), potassium tetraoxalate ( $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ), and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) were investigated for the Al and Fe extraction process from NIST SRM 600 – Australian Darling range bauxite ore. More than 90% of Al and Fe was extracted into the aqueous phase in less than 2 h with 0.50 M  $\text{C}_2\text{O}_4^{2-}$  for all three reagents. The Fe and Al can be selectively precipitated by hydrolyzing the aqueous phase. By acidifying the Al and Fe free filtrate, 80% of the  $\text{C}_2\text{O}_4^{2-}$  can be precipitated as  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . Greater than 90% of the aqueous acid can also be recycled using a cation exchange resin. The proposed closed-loop process is an energy-efficient, cost-effective, environmentally-friendly route for extracting Al and Fe from bauxite ore.

**KEYWORDS.** bauxite, metal extraction, ore refining, oxalic acid, red mud, leaching

## INTRODUCTION

Aluminum is a lightweight, durable, recyclable metal with its primary use in the production of high strength alloys in combination with other metals like Ni, Zn, Cu, and Mn. These alloys are used in a broad range of industries that vary from automobile manufacturing to aeronautical applications.<sup>1</sup> The primary source of

Al is aluminum oxide (alumina) present in bauxite ore. More than 90% of globally mined bauxite is used for Al production. On average, a bauxite ore contains 30-60 wt% of alumina, the rest being a mixture of iron oxides and quartz.<sup>2</sup> Commercially, bauxite is refined using the Bayer process to produce smelter-grade alumina that is then converted to Al metal using the Hall-Héroult process.<sup>1, 3</sup>

In bauxite, Al is present in the form of aluminum oxide trihydrate like gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  or  $\text{Al}(\text{OH})_3$ ) and monohydrate minerals such as boehmite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\gamma\text{-AlO}(\text{OH})$ ) and diasporite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\alpha\text{-AlO}(\text{OH})$ ). Other minerals which can be found in bauxite include hematite ( $\text{Fe}_2\text{O}_3$ ) and quartz ( $\text{SiO}_2$ ). The Bayer process involves the digestion of crushed bauxite in concentrated NaOH solution at high temperatures. The Al present in the ore reacts with NaOH to form water soluble sodium aluminate ( $\text{NaAlO}_2$ ) leaving behind an insoluble solid residue (red mud). However, the dissolution of  $\text{SiO}_2$  and Al in concentrated NaOH solution makes the Bayer process inefficient for low-grade bauxite ores (greater than 10 wt%  $\text{SiO}_2$  content).

The bauxite refining industry faces a global environmental issue because of the disposal problems associated with the caustic bauxite tailings commonly referred to as red mud.<sup>4-5</sup> The red mud is discharged from the process as an alkaline slurry with a pH > 12. It primarily consists of bauxite tailings like iron oxide ( $\text{Fe}_2\text{O}_3$ ) and quartz ( $\text{SiO}_2$ ).<sup>6</sup> Typically, about 1.0-1.5 tons of red mud are produced per ton of alumina in the Bayer process.<sup>7</sup> For the disposal of red mud, methods like landfills, deep-sea dumping, or storage in open ponds or reservoirs are utilized. The high alkalinity of the red mud pollutes the land and threatens plant growth and wildlife.<sup>8-9</sup> With the growing demand for Al, the disposal methods of red mud are an issue that needs global attention. In the past two decades, there have been numerous red mud incidences because of its disposal. The most disastrous incident occurred in Hungary in 2010, when the Ajka refinery dam collapsed, resulting in red mud flooding the nearby area. The release of approximately 1 million cubic meters of red mud contaminated more than 40 square kilometers of land and led to 9 deaths and 122 severely injured.<sup>10-11</sup>

To solve the problems associated with red mud, either environmentally-friendly techniques have to be utilized to dispose of red mud responsibly, or it can be eliminated at the source by developing a closed-loop bauxite refining process. Numerous researchers have worked on the recovery of valuable metals from red mud using both pyrometallurgy and hydrometallurgy.<sup>12-16</sup> Pyrometallurgy is energy intensive, whereas hydrometallurgical processes using inorganic acids (e.g., sulfuric acid and nitric acid) poses significant environmental risk from the emission of  $\text{SO}_x$  and  $\text{NO}_x$ . The large amount of acid initially involved for neutralizing the caustic red mud and the handling of effluents create an additional burden on the red mud processing.<sup>10</sup> In this work, we are investigating a closed-loop hydrometallurgical approach for bauxite refining with minimal waste to eliminate the concerns associated with red mud. In our alternative approach for bauxite refining, oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) and two of its derivatives with potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ): potassium hydrogen oxalate ( $\text{KHC}_2\text{O}_4$ ) and potassium tetraoxalate ( $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ) are investigated as reagents to extract Al and Fe from bauxite.

The oxalate ion is a bidentate ligand with excellent chelation properties. The  $\text{H}_2\text{C}_2\text{O}_4$  and its derivatives ( $\text{KHC}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ) utilize the chelation property along with the acidity to extract metals from the metal oxides. Previously,  $\text{H}_2\text{C}_2\text{O}_4$  has been used to extract metals from various sources ranging from spent lithium-ion battery cathodes<sup>17-18</sup> to ores such as laterite<sup>19</sup> and scheelite.<sup>20-21</sup> Corbin et al. developed two environmentally-friendly closed loop processes for extraction of Fe and Ti from ilmenite using ammonium hydrogen oxalate ( $\text{NH}_4\text{HC}_2\text{O}_4$ )<sup>22</sup> and trimethylammonium hydrogen oxalate ( $(\text{NH}(\text{CH}_3)_3)\text{HC}_2\text{O}_4$ ).<sup>23</sup> The  $\text{H}_2\text{C}_2\text{O}_4$  and its derivatives can be advantageous for metal separations in aqueous medium. Most of the divalent ( $\text{M}^{2+}$ ) metal ions are known to form insoluble metal oxalate compounds, whereas monovalent ( $\text{M}^+$ ) and trivalent ( $\text{M}^{3+}$ ) metal ions form soluble metal oxalates.<sup>24-25</sup> The difference in the aqueous solubility can be utilized to separate metal oxalate compounds.

In this study, a standard bauxite material from the Australian Darling range (NIST SRM600) has been used to investigate the feasibility of a closed-loop Al and Fe recovery process using  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{KHC}_2\text{O}_4$ , and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . The separation of  $\text{SiO}_2$  from  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  is a major advantage of using an acidic process. The Al and Fe from their respective metal oxides are leached into the aqueous phase, whereas silica remains in the solid phase. The Al and Fe extracted in the aqueous phase can be separated using

selective hydrolysis, and pH conditions have been optimized for efficient separation. However, the  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4$  are more expensive than inorganic acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .<sup>17</sup> To offset the cost of oxalate-based acids and make this process economical, an ion-exchange resin and a pH-based separation have been developed to recover the oxalate-based acids in their original form. To the best of our knowledge, this is the first study on extraction of metals from bauxite using oxalic acid and its derivatives. This novel closed-loop process is an environmentally-friendly and economical route for recovering Al and Fe from bauxite ore.

## EXPERIMENTAL SECTION

**Materials.** In this study, NIST SRM 600 – Bauxite, Australian-Darling Range,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (ACROS Organics, 99.5%),  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (Alfa Aesar<sup>TM</sup>, 98.8%), and deionized water were used for the metal extraction experiments. Potassium hydroxide, (KOH Pellets, Fisher Chemical) and Fe metal powder (20 mesh, Alfa Aesar<sup>TM</sup>, 99%) were used for metal precipitation and hydrolysis, respectively. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , Fisher Scientific, 98%) was used for acidification and regeneration of oxalate.

**Reactor Setup and Sampling.** The metal extraction experiments were carried out in a 1-L glass reactor attached to a 5-neck Duran<sup>®</sup> head with two thermocouples, an electric agitator, and a reflux condenser. The reactor was enclosed in a heating jacket controlled by a set of PID temperature controllers. The reflux condenser was connected to a chiller operating at 4 °C to avoid water loss during the experiment. A detailed reactor schematic can be found in our previous work.<sup>17</sup> The reactor temperature and agitation speed ( $N_s$ ) were set at 98 °C and 600 rpm, respectively, for all the experiments in this work. The temperature and agitation speed values were optimized to maximize the kinetics and avoid any diffusion limitation. Samples were withdrawn from the reactor at specific intervals using a 20 cm long needle connected to a 5 mL syringe. The withdrawn samples were centrifuged in a Falcon<sup>®</sup> tube for 5 min at  $N_s = 4000$  rpm to separate out the solids. The aqueous phase was diluted with 5 wt% nitric acid solution at a ratio of 1:10 for the measurement of Al and Fe concentrations.

**Metal Extraction, Hydrolysis, and Acid Regeneration.** Metal extraction experiments were carried out by mixing the oxalate reagents and heating them to a set temperature and then adding the required amount of bauxite. Aqueous  $\text{H}_2\text{C}_2\text{O}_4$  with or without  $\text{K}_2\text{C}_2\text{O}_4$  was used in each experiment. The  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4$  molar ratio is critical for the synthesis of  $\text{KHC}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . The reaction parameters for an efficient hydrometallurgical extraction are the acid concentration, temperature, solid-to-liquid ratio (S/L), and agitation speed. As mentioned in the previous section, the temperature and agitation speed were kept constant, while the effect of acid concentration was studied for all three oxalate reagents ( $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{KHC}_2\text{O}_4$ , and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ). The effect of increasing the S/L ratio was studied only with  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . Once the Al and Fe metals were extracted into the aqueous phase, the Fe was precipitated as  $\text{Fe}(\text{OH})_3$  via hydrolysis by increasing the pH using KOH. After removal of the Fe, the Al was precipitated from the solution by lowering the pH to an appropriate range by adding either  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{C}_2\text{O}_4$ . The specific range of pH for efficient precipitation of Al and Fe is discussed in the results and discussion section. The precipitation experiments were performed at 20 °C to maximize the precipitation efficiency using minimum energy.

The oxalate reagents were regenerated using two methods. The first approach involved using a strong acid cation exchange resin such as Amberlyst-15 H-form to decrease the pH. In this work, a batch process was used for the acid regeneration by mixing the activated resins with the filtrate in a benchtop shaker while monitoring the pH. After achieving the desired pH, the resins were regenerated by soaking them in a 1 M sulfuric acid solution for 24 h. In the presence of a strong acid, the resins regain their initial H-form. The regenerated resins were washed with DI water until the effluent was pH neutral before performing another ion exchange. The washing step removed any excess acid present on the resin beads. The washed and regenerated resins can be repeatedly used for additional metal precipitation. The second method for regenerating the oxalate reagents involved acidification of the filtrate post metal precipitation to the initial pH using  $\text{H}_2\text{SO}_4$ . The acidification will precipitate either  $\text{KHC}_2\text{O}_4$  or  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ , depending on the pH range. To minimize the amount of water added, 98 wt%  $\text{H}_2\text{SO}_4$  was used in the acidification process. This pH-based process utilizes solubility differences for separation and is discussed in detail in the results

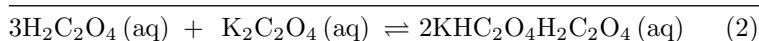
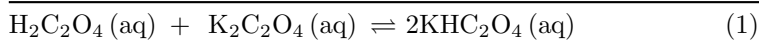
and discussion section.

**Characterization.** The metal concentrations in the solid and aqueous phase were measured using an inductively coupled plasma – optical emission spectrometer (ICP-OES). A Varian/Agilent 725 ES ICP-OES with simultaneous CCD detector was used for the measurements, and a Varian/Agilent SP3 autosampler was used to sequence multiple samples. The aqueous phase samples were diluted 100 times with 5 wt% HNO<sub>3</sub> before analyzing them by ICP. Elemental compositions of the solid phases were identified using X-Ray fluorescence (XRF) using a Malvern Panalytical Zetium (1 kW) instrument with a Rh anode and a 75 µm Be window with a duplex detector. Phase identification and crystallinity measurements were performed on a Bruker D2 phaser powder X-ray diffraction (PXRD) with a Co Kα radiation source ( $\lambda = 1.78897 \text{ \AA}$ ). The source voltage and current were set at 30 kV and 10 mA, respectively. The data were collected in the  $2\theta$  range of 10-70° with a step size of 0.02° and dwell time of 0.40 s per step. XRD patterns were analyzed using MDI Jade 6 software.

## RESULTS AND DISCUSSION

**Synthesis of Potassium Hydrogen Oxalate and Potassium Tetraoxalate.** H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is a diprotic acid with  $\text{pK}_{a1} = 1.23$  and  $\text{pK}_{a2} = 4.19$  at 20 °C. Both KHC<sub>2</sub>O<sub>4</sub> and KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> contain the binoxalate anion (HC<sub>2</sub>O<sub>4</sub><sup>−</sup>). Based on the speciation of oxalic acid, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is the predominant species below a pH = 1.23, HC<sub>2</sub>O<sub>4</sub><sup>−</sup> is the predominant species between pH = 1.23 and 4.19, and C<sub>2</sub>O<sub>4</sub><sup>2−</sup> is the predominant species above pH = 4.19.<sup>24</sup> The KHC<sub>2</sub>O<sub>4</sub> can be synthesized using a 1:1 molar ratio of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, as shown in eq 1. The KHC<sub>2</sub>O<sub>4</sub> is sparingly soluble in the resulting solution shown in eq 1 at 20 °C and a white precipitate was observed. The precipitate was filtered and identified as KHC<sub>2</sub>O<sub>4</sub> using PXRD.

KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is another derivative of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> that can be synthesized by mixing H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in a 3:1 molar ratio, as shown in eq 2. The KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was also found to be sparingly soluble in the resulting solution shown in eq 2 at 20 °C. A white precipitate was observed, filtered, and identified using PXRD as KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. These two derivatives provide an alternative to H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with moderate acidity and similar chelation properties. The low solubility of these acids in comparison to the H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> provides a convenient means to recover the acids after metal extraction. The details for the acid recovery will be discussed in the next section.



The solubilities of KHC<sub>2</sub>O<sub>4</sub> and KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were measured as 5.8 g and 3.0 g per 100 mL of water at 20 °C, respectively. The NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> and NaHC<sub>2</sub>O<sub>4</sub> were synthesized for measuring the solubilities in water at 20 °C. The details on the synthesis of NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> and NaHC<sub>2</sub>O<sub>4</sub> can be found in the Supporting Information. The solubilities of common oxalate compounds are compared in Table 1. The potassium-based oxalate compounds are unique because of the low solubility of KHC<sub>2</sub>O<sub>4</sub> and KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and the high solubility of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The high solubility of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is critical for separating pure metals (e.g. Al and Fe) during the hydrolysis step without any impurity.

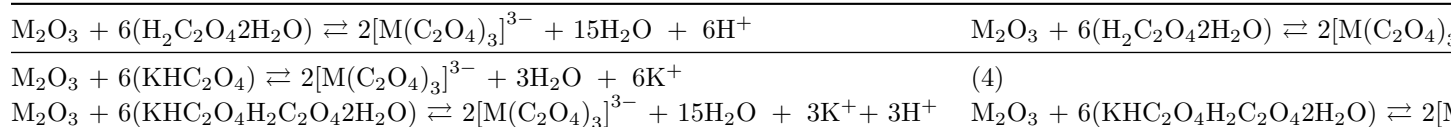
**Table 1.** Solubilities of common oxalate compounds relevant to this work.

Compound Formula	Aqueous solubility at 20 °C (g/100 ml)	Reference
NH <sub>4</sub> HC <sub>2</sub> O <sub>4</sub> ·0.5H <sub>2</sub> O	12.03 ± 0.42	This work
KHC <sub>2</sub> O <sub>4</sub>	5.73 ± 0.33	This work
KHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	2.97 ± 0.20	This work
NaHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.8 ± 0.22	This work
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	36.4	26

Compound Formula	Aqueous solubility at 20 °C (g/100 ml)	Reference
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	13.3	26
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	5.20	26
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	3.61	26

**Metal Extraction using Oxalate Reagents.** To understand the extraction of metals from NIST SRM 600 bauxite ore using aqueous H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (OA), KHC<sub>2</sub>O<sub>4</sub> (KHO) and KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (KTO), the temperature, agitation speed, and S/L ratio were kept constant at  $T = 100$  °C,  $N_s = 600$  rpm, and 15 g/L respectively, for all the experiments in this section unless specified otherwise. The S/L ratio can be optimized after understanding the mechanism. NIST SRM 600 bauxite contains Al in the form of gibbsite (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O), along with hematite (Fe<sub>2</sub>O<sub>3</sub>) and quartz (SiO<sub>2</sub>). A significant difference between the three oxalate reagents is the reaction pH. The OA is the most acidic, followed by the KTO and then KHO. The acidity of the reagent is critical for breaking the metal-oxygen bonds via hydrogen bonding that initiates the extraction of metals from metal oxides.<sup>27</sup> Figure 1a summarizes the Al and Fe extraction kinetics for NIST SRM 600 bauxite using OA.

The Fe extraction rate was significantly improved by increasing the OA concentration from 0.50 M to 0.75 M, whereas the Al extraction rate increased slightly. The Al extraction rate was faster than Fe, at both 0.50 M and 0.75 M OA, indicating a preference towards Al in the acidic pH range of 0.75-1.2. Greater than 90% of the Al was extracted in 1 h for at both 0.50 M and 0.75 M OA, while about 1.5 h was required for extracting 90% of the Fe. However, when similar extractions were performed using 0.50 M KHO and 0.75 M KHO (Figure 1b), the rate of Fe extraction was faster than Al. For both 0.50 M and 0.75 M KHO, less than 1 h was required to extract greater than 90% of the Fe. This observation indicates the importance of the HC<sub>2</sub>O<sub>4</sub><sup>-</sup> in Fe extraction. The KHO behaves as a pH buffer; therefore, when increasing the concentration of KHO, the pH remains the same, and no significant changes in metal extraction kinetics were observed. OA is the most acidic and effective at Al extraction from bauxite ore; however, the difficulty is regenerating the acid after precipitation of the Al and Fe. For this reason, the moderately acidic KTO is the preferred acid, which can be easily regenerated after Al and Fe precipitation. The stoichiometric reactions for the extraction of trivalent metal (M<sup>3+</sup> like Al<sup>3+</sup>, Fe<sup>3+</sup>) from its oxide (M<sub>2</sub>O<sub>3</sub>) using OA, KHO and KTO are shown in eqs 3-5.



KTO is a double salt of OA and KHO and comprises two moles of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> per mole of KTO. Hence, 0.25 M KTO (0.50 M C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) was used to perform the Al and Fe extraction from NIST SRM 600 bauxite at a 15 g/L S/L ratio. In the KHO study, no significant difference was observed in the rate of metal extraction at higher C<sub>2</sub>O<sub>4</sub><sup>2-</sup> concentration due to essentially the same pH; therefore, only 0.25 M KTO was studied in detail. In Figure 1a and 1b, the 0.50 M C<sub>2</sub>O<sub>4</sub><sup>2-</sup> concentration led to an efficient extraction of Fe and Al using 15 g/L S/L ratio of ore; therefore, a higher S/L ratio of 20 g/L with 0.25 M KTO was attempted, as shown in Figure 1c. The Al and Fe extraction kinetics for 20 g/L was slower in comparison to 15 g/L experiments because of the decreased concentration of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> per metal ion. However, greater than 95% of Al and Fe was extracted in 2.5 h at 20 g/L S/L ratio, which makes this process energy-efficient. An important observation was the rates of Al extraction for OA, KTO, and KHO at the 0.50 M C<sub>2</sub>O<sub>4</sub><sup>2-</sup> concentration were similar (Figure 1d), which confirms the negligible effect of pH on Al extraction kinetics. To understand this phenomenon in more detail, ore was digested in 0.50 M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and no Al extraction was observed, confirming the importance of acidity to initiate the extraction. The elemental composition shown in Table 2

after the extraction experiments indicates less than 10% of Al and 2% of Fe remain in the solid residue. The typical mass of solid residue recovered was 2.5 g from 15 g of ore digested in 1 L of acid. From the elemental composition of the ore and remaining solid residue shown in Table 2, it can be seen that in addition to Al and Fe, some other metals such as Zr and Mg are also leached into the aqueous phase. The residues recovered in the experiments shown in Figure 1a-1d were also confirmed using PXRD to be primarily quartz ( $\text{SiO}_2$ ). The PXRD patterns for the NIST SRM 600 and the solid residues from the bauxite digestion using 0.50 M OA, 0.50 M KHO, and 0.25 M KTO are shown in Figures S1 and S2, respectively.

**Table 2.** Elemental composition of NIST SRM 600 and the solid residues remaining after refining of NIST SRM 600.

Extraction reagent and conditions	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
	Al	Fe	Si	Ti
NIST SRM 600	33.80	13.52	6.20	0.87
0.50 M KHO – 15 g/L	9.70	1.06	34.05	2.81
0.75 M KHO – 15 g/L	8.00	0.94	35.61	2.56
0.25 M KTO – 15 g/L	9.16	1.09	34.51	3.17
0.25 M KTO – 20 g/L	9.45	2.05	33.39	3.23

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image1.emf available at <https://authorea.com/users/419615/articles/526058-extraction-of-aluminum-and-iron-from-bauxite-a-unique-closed-loop-ore-refining-process-utilizing-oxalate-chemistry>

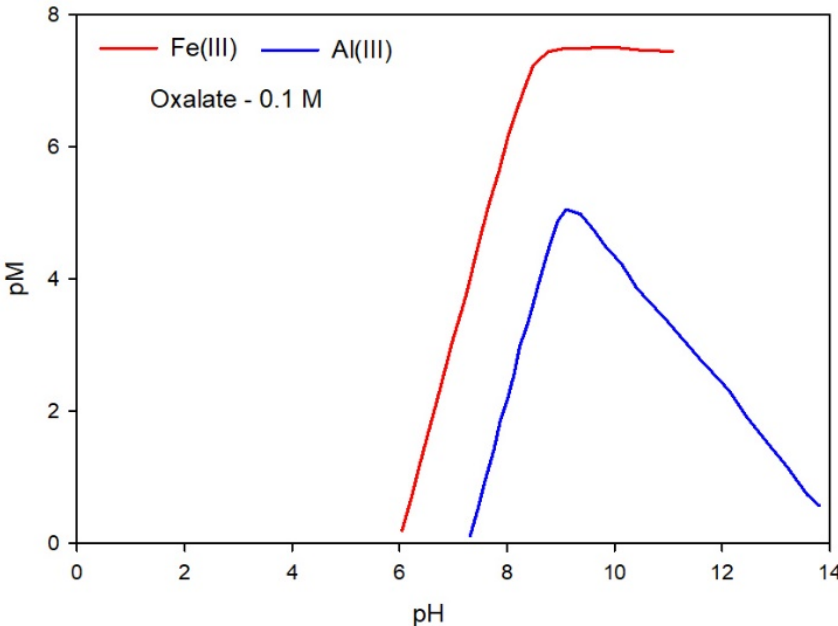
**Figure 1.** Metal concentration for Al and Fe as a function of time in the aqueous phase for (a) 0.50 M and 0.75 M OA at  $T = 100^\circ\text{C}$ ,  $S/L = 15\text{ g/L}$  and  $N_s = 600\text{ rpm}$  (b) 0.50 M and 0.75 M KHO at  $T = 100^\circ\text{C}$ ,  $S/L = 15\text{ g/L}$  and  $N_s = 600\text{ rpm}$  (c) 0.25 M KTO at  $T = 100^\circ\text{C}$ ,  $S/L = 15\text{ g/L}$  and  $20\text{ g/L}$  and  $N_s = 600\text{ rpm}$  (d) 0.50 M OA, 0.50 M KHO and 0.25 M KTO at  $T = 100^\circ\text{C}$ ,  $S/L = 15\text{ g/L}$  and  $N_s = 600\text{ rpm}$

**Separation of Al and Fe from the Aqueous Phase.** The oxalate-based acids (OA, KHO, and KTO) provide an efficient extraction (greater than 95 wt%) for Al and Fe into the aqueous phase and an easy separation for the remaining solid residue which is primarily made of  $\text{SiO}_2$ . The next step is to efficiently recover the Al from the aqueous phase and minimize any co-precipitation of Fe or other impurities.

The Al and Fe in the NIST SRM 600 bauxite ore are both present in the +3 oxidation state. The Al and Fe can be hydrolyzed to precipitate as metal hydroxides. To selectively precipitate these metals the pH must be optimized. The “Atlas of metal-ligand equilibria in aqueous solutions” by J. Kragten provides the pH range required for precipitation of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  using  $0.1\text{ M C}_2\text{O}_4^{2-}$  solution.<sup>28</sup> The  $\text{Al}(\text{OH})_3$  is amphoteric in nature and can act as a Lewis acid that binds with  $\text{OH}^-$  ions to form a water-soluble  $\text{Al}(\text{OH})_4^-$  ion.<sup>29</sup> Hence, the concentration of  $\text{Al}^{3+}$  metal in the aqueous phase decreases during hydrolysis up to about a pH = 9, but starts increasing as precipitate dissolves at higher pH. The  $\text{Fe}(\text{OH})_3$  precipitation begins before the  $\text{Al}(\text{OH})_3$  but is not amphoteric and can be precipitated efficiently at high pH.

To precipitate Al and Fe effectively without any impurities, the basicity of the aqueous phase was increased to a pH of about 14 using KOH. To avoid the precipitation of insoluble metal oxalates, the base KOH is preferred versus NaOH. The high solubility of  $\text{K}_2\text{C}_2\text{O}_4$  (Table 1) enables the efficient precipitation of Al and Fe. Greater than 99% of the Fe precipitates at a pH of about 14, while the majority of the Al remains in solution. Any remaining Al can be separated by lowering the pH to about 10.5 using  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{C}_2\text{O}_4$ . The approach is described in Table 3 for filtrate recovered after refining bauxite ore using OA, KTO, and KHO. Under these concentrations, a pH = 10.5 was found to be optimum for Al precipitation. Using this approach, Al can be precipitated without any Fe impurity. The elemental composition of Al and Fe precipitates recovered from the aqueous filtrate of 0.25 M KTO extraction are shown in Table 4. A similar

elemental composition was observed for the precipitates recovered from the aqueous filtrate after extracting Al and Fe using 0.50 M OA and KHO. It should be noted that around 10% of Al precipitates with the Fe. To recover this additional Al, the Fe precipitate can be dissolved in an acidic oxalate solution (similar to the oxalate reagent initially used), and the approach described in Table 4 can be repeated to separate the remaining Al without any Fe impurity.



**Figure 2.** pM versus pH diagram for Fe(III) and Al(III) with 0.1 M oxalate ions. pM is defined as the negative log of the metal ions concentration in the aqueous phase.

**Table 3.** Methodology for selective precipitation of Al and Fe.

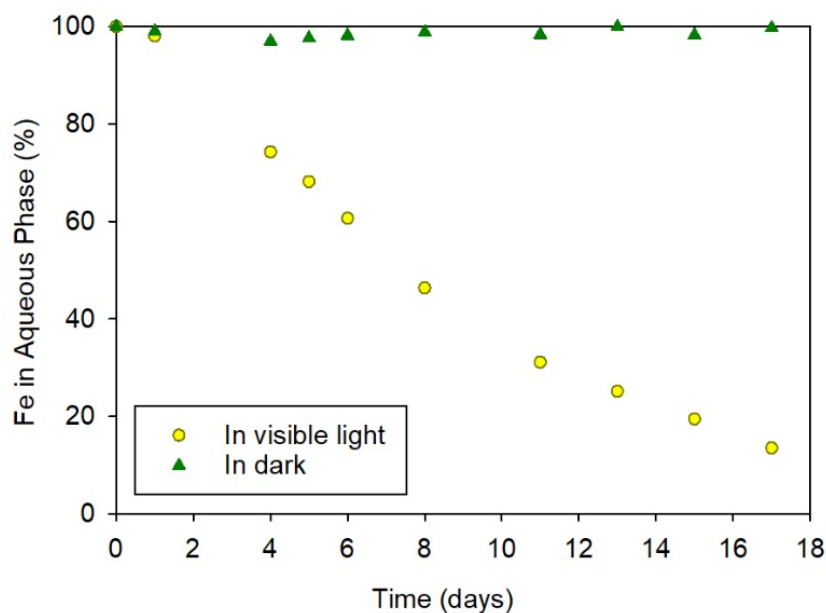
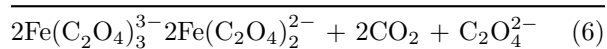
Acid concentration (Initial pH)	Procedure (Final pH)	Fe remaining in the aqueous phase (%)	Al remaining in the aqueous phase (%)
0.50 M OA (0.93)	KOH addition (13.87)	0.001	93.2
	H <sub>2</sub> SO <sub>4</sub> addition (10.52)	0.002	0.16
0.25 M KTO (1.51)	KOH addition (13.85)	0.002	92.8
	H <sub>2</sub> SO <sub>4</sub> addition (10.56)	0.002	0.15
0.50 M KHO (2.47)	KOH addition (13.88)	0.001	92.6
	H <sub>2</sub> SO <sub>4</sub> addition (10.48)	0.001	0.24

**Table 4.** Elemental composition of Al and Fe precipitate recovered from the filtrate of 0.25 M KTO experiment at  $T = 100\text{ }^{\circ}\text{C}$ ,  $S/L = 15\text{ g/L}$ , and  $N_s = 600\text{ rpm}$ .

Precipitate from the aqueous filtrate of 0.25 M KTO extraction	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
	Al	Fe	Si
pH = 13.85	11.06	27.29	1.49
pH = 10.56	33.89	0.05	0.61

Note: ND - Not determined

Iron precipitation (yellow precipitate) was also observed in the presence of visible light when aqueous filtrates were stored in clear glass bottles. This yellow precipitate was confirmed as  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  using PXRD (Figure S3). The photoreduction of iron(III) oxalate complex to iron(II) oxalate complex has been reported by numerous researchers.<sup>30-32</sup> Mangiante et al. described this photoreduction through eq 6.<sup>32</sup> The observation of yellow precipitate from the complex could be attributed to the low pH (pH = 0.93-2.47) of the aqueous phase. In this pH range  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{HC}_2\text{O}_4^-$  are the predominant forms of oxalate ions.<sup>24</sup> The lack of  $\text{C}_2\text{O}_4^{2-}$  combined with the low solubility of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.078 g/100 g  $\text{H}_2\text{O}$  at 20 °C)<sup>26</sup> leads to the precipitation of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .<sup>33</sup> The kinetics of the photoreduction of  $\text{Fe}^{3+}$  was slow but efficient, as shown in Figure 3. It is clear from Figure 3 and eq 6 that to avoid any Fe precipitation and decomposition of  $\text{C}_2\text{O}_4^{2-}$  bauxite filtrates should be stored in the dark.

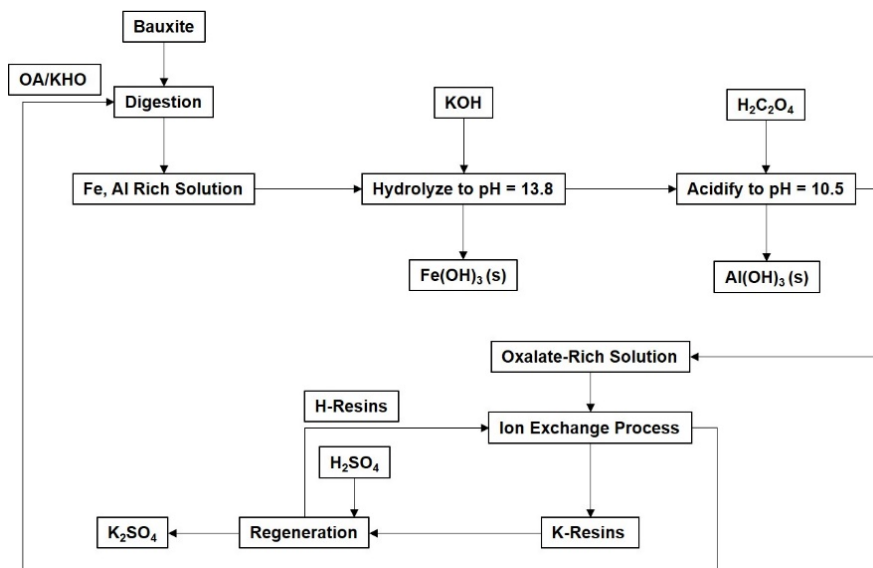


**Figure 3.** Effect of visible light on the concentration of Fe in the aqueous phase.

**Recycling of Oxalic Acid and its Derivatives.** A critical step for improving the economics of a metal extraction process is the recycling of the acids used for leaching. For the regeneration of KTO, KHO and OA, an ion-exchange resin was used to regenerate the acid and recycle it for future metal extraction. The precipitation of Al and Fe using KOH and  $\text{H}_2\text{C}_2\text{O}_4$  produces  $\text{K}^+$  ions as the major cation in the aqueous phase. A strong acid cation exchange resin like Amberlyst 15 H-form was used to exchange the  $\text{K}^+$  with  $\text{H}_3\text{O}^+$  ions for regeneration of the oxalate reagents used in this study. The overall closed-loop process is shown in Figure 4. The amount of activated H-form resin added to the aqueous phase (containing  $\text{K}^+$ ) determines the final pH. The KHO was regenerated to a pH of about 2.50 and KTO is produced at a pH of about 1.50. The regeneration of OA required a pH of about 1.0 and utilized the most resin. The ideal pH after the ion-exchange treatment should be close to the initial pH needed for the metal extraction process. A small amount of  $\text{H}_2\text{C}_2\text{O}_4$  or  $\text{K}_2\text{C}_2\text{O}_4$  is likely required to achieve the same starting oxalate concentration, but overall a significant amount of oxalate can be recycled; therefore, reducing the amount of fresh acid required

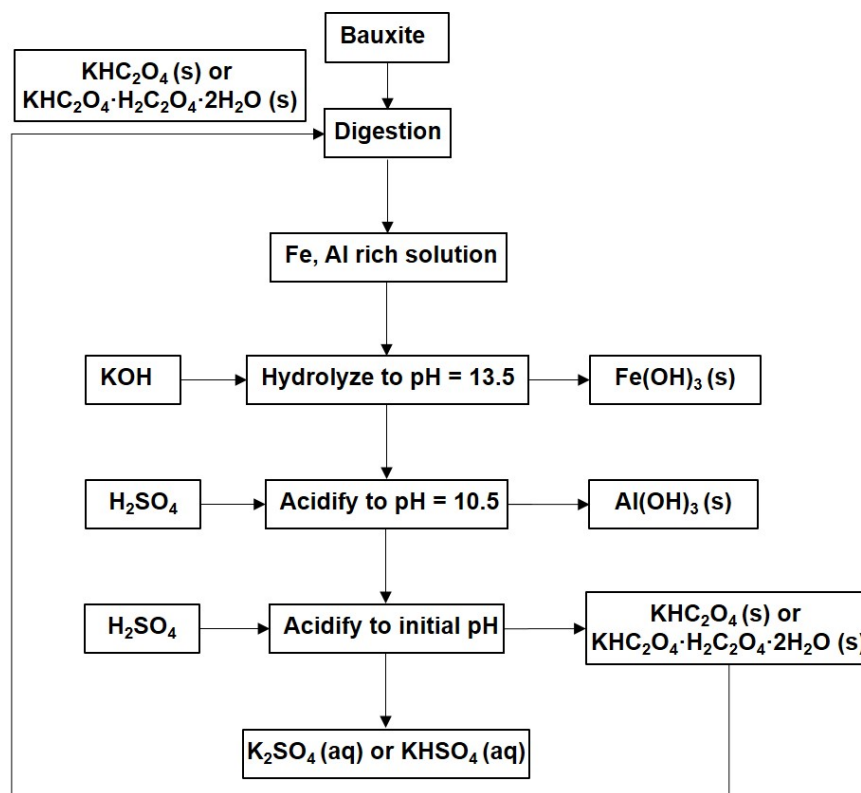


and closing the loop on acid recovery and reuse. In the preliminary studies, around 30 g of Amberlyst-15 H-form (dry) was used to regenerate OA (pH = 1.2) from 1-L of filtrate recovered after Al precipitation at a pH of about 10.9. The recovery process requires an excess of ion-exchange resin and water; however, the preliminary results are promising, and the work to optimize this process is ongoing.



**Figure 4.** Flowsheet for the proposed closed-loop bauxite refining process using ion-exchange resins.

The alternative method for regenerating the oxalate-based reagents involves the acidification of the post precipitation filtrate using H<sub>2</sub>SO<sub>4</sub>. Similar to the ion-exchange resin approach, the final pH is critical in achieving the regenerated oxalate reagent. In this approach, the low solubility of potassium containing oxalate reagents is beneficial for precipitation, and the precipitated reagents can be efficiently filtered and separated. For the operating conditions described in this work, the aqueous phase will be oversaturated with KHO and KTO and undersaturated for OA; therefore, only KHO and KTO will precipitate. In our preliminary studies to acidify the post precipitate filtrate to a pH = 2.5 using H<sub>2</sub>SO<sub>4</sub>, approximately 65% of the initial C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion was recovered in the form of KHO. Decreasing the pH to 1.5 led to 80% of the initial C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion recovery in the form of KTO. The precipitates were confirmed as KHO and KTO using PXRD, as shown in Figure S4 and Figure S5, respectively. The closed-loop process is summarized in Figure 5. Decreasing the pH below 1.5 led to precipitate dissolving due to the higher solubility of OA compared to KTO. The approach shown in Figure 5 has the advantage because no ion exchange resin is required, but the regeneration of OA is a drawback.



**Figure 5.** Flowsheet for the proposed bauxite refining process using oxalate precipitation.

## CONCLUSIONS

Commercially valuable metals like Al and Fe can be recovered efficiently from NIST SRM 600 bauxite ore using an environmentally-friendly process based on oxalate chemistry. In this work, an efficient Al and Fe extraction process using three oxalate reagents: H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, KHC<sub>2</sub>O<sub>4</sub>, and KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> has been demonstrated. The three oxalate reagents were synthesized using various molar ratios of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The amount of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> determines the reaction pH and the rate of metal dissolution. The kinetics of Al extraction had a negligible dependence on the pH; however, the presence of H<sup>+</sup> ions are necessary for the metal dissolution. The kinetics of Fe extraction was dependent on pH and the fastest rate was measuring for KHO at a pH = 2.50. KHO is an effective and safe acid for Al and Fe extraction from bauxite ore compared with the strong acids and bases currently used in the Bayer process. The amphoteric behavior of Al(OH)<sub>3</sub> allows selective precipitation of Fe at a pH = 13.80 and Al can be subsequently precipitated by acidifying the filtrate to a pH = 10.50. The efficient extraction of Al and Fe from bauxite ore produces only quartz (SiO<sub>2</sub>) as the final residue.

In the described processes, 98-99% pure alumina can be produced. A critical step in the proposed process is the recovery and recycling of oxalate. After precipitating and separating the metals, an ion-exchange resin process was developed to regenerate the H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, or KHC<sub>2</sub>O<sub>4</sub> in solution. An alternative approach that acidifies the precipitation filtrate takes advantage of the lower solubility of KHC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and KHC<sub>2</sub>O<sub>4</sub>. Both reagents can be precipitated from the aqueous solution and recovered as solids. The closed-loop process utilizing oxalate chemistry does not produce any hazardous waste, unlike the alkaline red mud produced in the Bayer process. The simple and novel process using the combination of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> provides a safe, efficient, sustainable, and environmentally-friendly route for recovering commercially valuable metals such as Al and Fe from bauxite ore.

## SUPPORTING INFORMATION

The supporting information is available free of charge on the journal website.

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