

Leaching Kinetics of Iron from Electric Arc Furnace Slag (EAFS)

Faizatul Syazwani Zulkifili¹, Norhaslinda Nasuha^{1,2}, Siti Wahidah Puasa^{1,3}, Hawaiah Imam Maarof^{1,2*}

¹School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Selangor, Malaysia

²Hybrid Nanomaterials, Interfaces & Simulation (HYMFAST), School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Pulau Pinang, Malaysia

³Integration Separation Technology Research Group (i-STRonG), College of Engineering, Universiti Teknologi MARA, Selangor, Malaysia

*Corresponding Author

doi: <https://doi.org/10.21467/proceedings.141.2>

ABSTRACT

The steelmaking process produces a substantial amount of electric arc furnace slag (EAFS). Therefore, this present study conducted acid leaching, with and without the use of oxidants such as hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄), to increase the amount of iron (Fe) recovered from the EAFS. The effect that reagent concentration of 0.5-8.0 M, leaching temperatures of 50-90 °C, and oxidant concentrations of 0.1-2.0 M had on leaching activities were investigated. A temperature of 50 °C, a 5 M sulphuric acid (H₂SO₄) concentration, a 1 M hydrogen peroxide concentration, a leaching duration of 60 minutes, a 1:20 solid: liquid (S: L) ratio, and a 300-rpm stirring rate was found to yield the highest iron recovery. Three kinetics models; diffusion-controlled, chemical reaction-controlled and mixed-controlled model; were also investigated. The reaction was found to follow the chemical-reaction model as it yielded the highest square of the correlation coefficient (R², 0.9998). The activation energy of the chemical reaction-controlled model was +16.95 kJ/mol. During the cyclic voltammetry (CV) study, 0.1 M sodium chloride (NaCl) was added to the iron-rich leaching solution to act as a supporting electrolyte. Tests were then conducted at potential ranges of -1-1 V at a scan rate of 100 mV/s using screen printed carbon electrode (SPCE). The CV indicated that there were two distinct oxidation peaks (-1.5 and .5 V) and two distinct reduction (0.9 and -0.9 V) peaks occurred at all temperatures.

Keywords: Separation, electric arc furnace slag, reaction kinetics, recovery

1 Introduction

The infrastructure and construction sectors of Malaysia, a developing country, are currently undergoing tremendous development. However, steel is in high demand not only in Malaysia, but also globally. According to the World Steel Association, global crude steel production had surpassed 791.8 million tonnes as of May 2022. Meanwhile, the by-products of crude steel production; such as electric arc furnace slag (EAFS); are estimated to range between 11-20 kg/tonne of steel [1]. As EAFS is a solid waste by-product of the steelmaking processes, it contains a diverse range of metals. According to Lin, et al. [2], EAFS can contain up to 40% zinc and 50% iron in addition to several other harmful metals; such as lead, chromium, and cadmium. Bakkar [3] reports that EAFS comprises the metal oxides of iron, zinc, lead, chromium, and cadmium while Monosi, et al. [1] reports that EAFS is primarily composed of oxides, specifically iron (70%), calcium and silicon. Unfortunately, most metallurgical industries generate massive amount of hazardous waste that contain dissolved toxic metals.

Due to the limitations of current disposal methods, recycling is believed to be the most sustainable method of managing the large amounts of solid waste that the steelmaking industry generates. Leaching not only requires low energy consumption but is a less harmful method that is capable of facilitating highly selective metal recoveries [4, 5]. As Malaysia's current recycling rate is unsatisfactory, additional landfills have to be



© 2022 Copyright held by the author(s). Published by AIJR Publisher in the "Proceedings of International Technical Postgraduate Conference 2022" (TECH POST 2022) September 24-25, 2022. Organized by the Faculty of Engineering, Universiti Malaya, Kuala Lumpur, Malaysia.

Proceedings DOI: [10.21467/proceedings.141](https://doi.org/10.21467/proceedings.141); Series: AIJR Proceedings; ISSN: 2582-3922; ISBN: 978-81-957605-4-1

opened however, existing methods of disposing of this solid, be it landfills or incineration, have proven ineffective [6, 7]. As such, this solid waste has accumulated over the years as no effective countermeasures have been implemented. Therefore, Malaysia needs to position recycling as a beneficial option for both manufacturers and the community, which will ultimately lead to a better country.

Reusing slag in secondary applications is the most ostensible alternative to landfills. Nasuha, et al. [8] recycled EAFS for use as a catalyst in wastewater treatment and reported that thermally treated EAFS provided promising organic dye removal via a heterogeneous Fenton-like reaction. Meanwhile, Teo, et al. [9] examined the potential of recycling EAFS into value-added green products; such as aggregates, adsorbents in wastewater treatment, fertilizer, and raw materials for ceramic products. However, due to the complex composition of iron, the study failed to adequately address the selective recovery and maximization of the amount of iron in the final product. Although extant studies have examined iron leaching from EAFS [10], the leaching was conducted at a high temperature of 90 °C and over a longer reaction time of five hours. Furthermore, no study has examined the total dissolution of iron from EAFS with nitric acid as a leaching agent. Therefore, this present study endeavored to reduce the leaching duration and temperature of an existing leaching method as well as increase the amount of selective iron that can be used as a catalyst. As iron accounts for roughly half of the slag composition, this was deemed as an excellent method of recovering the most amount of iron at a lower cost.

2 Materials and Methods

2.1 Materials

Electric arc furnace slag (EAFS); a solid waste that forms in the furnace during the steel production; was obtained from a local steel company located in Penang. A particle size of 75 μm was used in all the leaching experiments. Sulphuric acid (H_2SO_4 , 98%), nitric acid (HNO_3 , 99.99%), hydrogen peroxide (H_2O_2 , 30%), and potassium permanganate (KMnO_4) were purchased from Sigma-Aldrich meanwhile hydrochloric acid (HCl , 37%) was purchased from Merck. All acids were used as is sans purification. Temperatures of 50-90 °C, lixiviant concentrations of 0.5-8 M and oxidant concentrations of 0.1-2 M were studied.

2.2 Leaching analysis

A PAN analytical, Epsilon 3-XL X-ray fluorescence (XRF) spectrometer was used to determine the mineral composition of the crushed raw EAFS. Two types of leaching analyses were conducted: oxidative and non-oxidative leaching. For the non-oxidative leaching analysis, 5 g of the powdered EAFS was added to a 100 mL of acid solution at a solid: liquid (S: L) ratio of 1:20 and a predetermined concentrations of 0.5 to 8.0 M. The mixture was then heated at 50 °C for 60 minutes before filtering. The filtrate was collected with a syringe then analysed using a Hach DR 2800™ spectrophotometer. Hach™ FerroVer® iron reagent powder pillows at concentrations ranging between 0.02-3.00 mg/L were used in the spectrophotometer at 510 nm to analyse the iron concentration of the leachate. Meanwhile, to analyse the oxidative leaching, hydrogen peroxide was added to the leaching medium as an oxidising agent and stirred at 300 rpm. The same process was repeated with potassium permanganate as an oxidant. Leaching experiments were conducted thrice for each oxidant to obtain an average value.

3 Theory and Calculation

3.1 Diffusion-controlled model

According to Nernst's theory of the boundary layer, leaching reactions are typically governed by the diffusion mechanisms that occur at the rate-determining stage [11]. Different forms of diffusion mechanisms could control the leaching kinetics such as a liquid boundary layer diffusion-controlled mechanism and inner diffusion-controlled mechanism. Equation 1 depicts the inner diffusion-controlled mechanism of spherical particles.

$$1 - 3(1 - \chi)^{\frac{2}{3}} + 2(1 - \chi) = k_p t \quad (1)$$

3.2 Chemical reaction-controlled model

Chemical reactions at the solid or liquid interfaces typically result in the formation of products around the unreacted core. As the rate at which the surrounding products form is slower than that of lixiviant diffusion, the surface reaction is regarded as the determining stage. Equation 2 depicts a model that assumes that the controlling rate is determined by a chemical reaction.

$$1 - (1 - \chi)^{\frac{1}{3}} = k_c t \quad (2)$$

3.3 Mixed-controlled model

The initial controlling mechanism of a reaction can be altered depending on the physical and chemical properties, such as the porosity and permeability, of the removed product layer. Equation 3 depicts a mixed-controlled model when the inner diffusion and chemical reaction mechanisms co-exist.

$$(1 - \chi)^{-\frac{1}{3}} + \frac{1}{3} \ln(1 - \chi) - 1 \quad (3)$$

4 Results and Discussion

4.1 XRF analysis

Table 1 lists the chemical composition of EAFS. Iron was found to be the third highest component alongside calcium, silicon, aluminium, and magnesium. The compositions predominantly contained iron, calcium, and silicon oxides as well as trace amounts of magnesium and manganese oxides. Nasuha, et al. [8] also reported similar EAFS chemical composition, with iron accounting for approximately 32.65 wt. %.

Table 1: The chemical composition of the EAFS

Component	CaO	Al ₂ O ₃	MgO	Fe ₂ O ₃	MnO	SiO ₂
wt. %	35.61	5.15	3.59	26.79	4.36	15.04

4.2 Leaching kinetics

Figure 1 depicts the iron leaching of the EAFS over a 180-minute period when nitric and sulphuric acid were used as leaching agents. As seen, iron leaching plateaued after 120 minutes indicating that it had reached its saturation point and that only negligible amounts of iron would leach out past this point. The maximum amount of iron recovered during 120 minutes of dissolution was +9600 and 10300 mg/L for sulphuric acid and nitric acid, respectively. The shrinking core model was used to fit the iron leaching efficiencies at different temperatures. A series of experiments were conducted at five different temperatures to investigate the effect of temperature and the reaction mechanisms as well as to calculate the activation

energy. Figures 2a-c were plotted and analysed using linear regression using Equations 1, 2, and 3, respectively. The R^2 of the diffusion-controlled, chemical reaction-controlled, and mixed-controlled were 0.8875-0.9872, 0.9391-0.9998, and 0.8882-0.9943, respectively. Therefore, the reaction that occurred between the iron and lixiviant followed the chemical reaction-controlled model as it had the highest R^2 value.

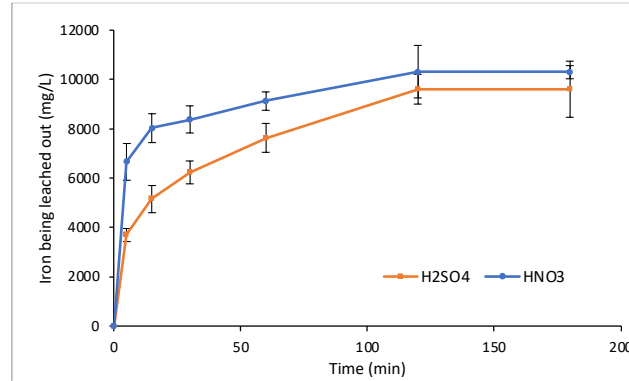


Figure 1: Iron leaching out of the raw EAFS

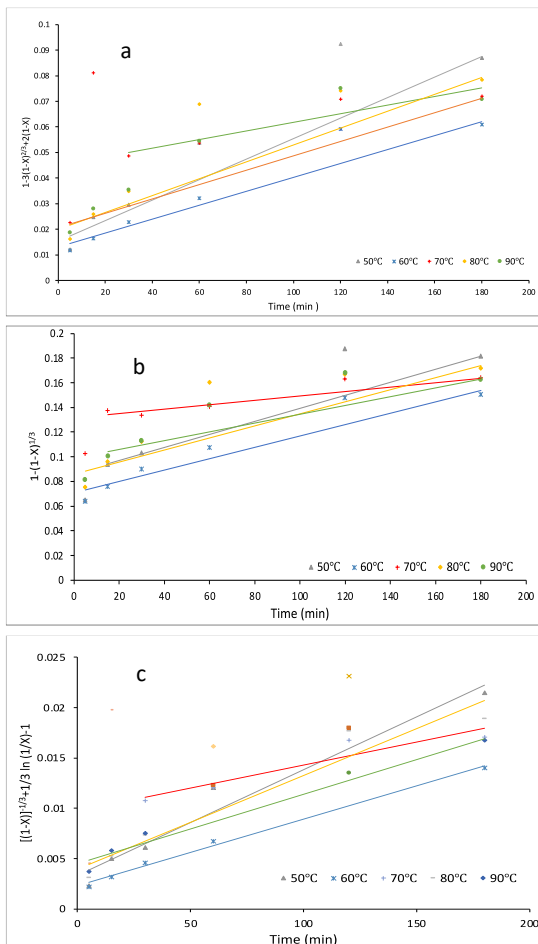


Figure 2: The linear fitting the reaction curves of the EAFS with different controlling processes (a) diffusion-controlled, (b) surface chemical reaction-controlled, and (c) mixed-controlled

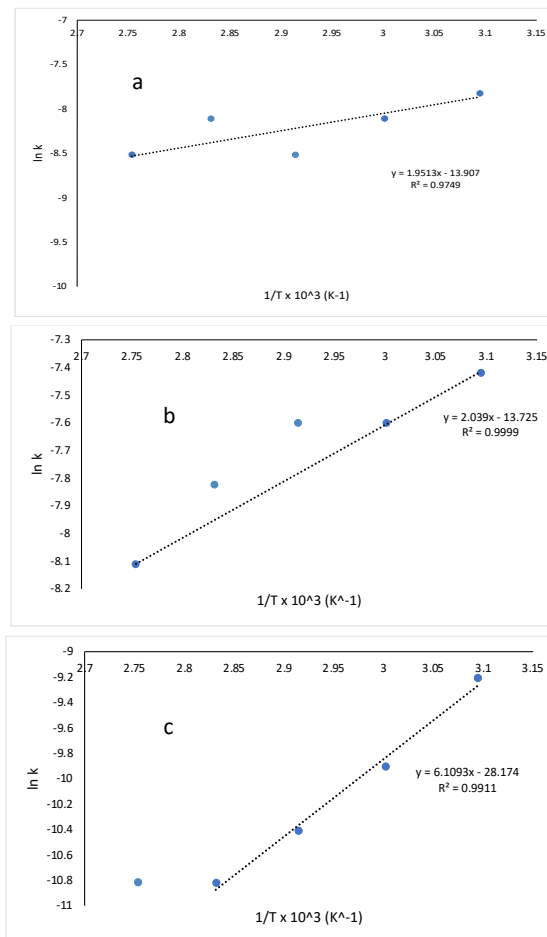


Figure 3: The Arrhenius plot of data in different control modes: (a) diffusion-controlled, (b) surface chemical reaction-controlled, and (c) mixed-controlled

As seen in Figure 3, the curves of the $\ln k$ versus $1/T$ were further plotted to evaluate the leaching kinetics in accordance with Equation 4. The activation energy of each control model was calculated using the slopes of Figures 3a-c. Table 2 summarises the activation energies.

Table 2: The results of the Arrhenius model parameter fitting results

Models	Reaction rate, k (10^3)	Correlation coefficient, R^2	Activation energy, $E_a/kJ.mol^{-1}$
Diffusion controlled	1.95	0.9749	16.22
Chemical reaction-controlled	2.04	0.9999	16.95
Mixed controlled	6.11	0.9911	50.79

The activation energies of the diffusion-controlled, surface chemical reaction-controlled, and mixed-controlled were 16.22, 16.95, and 50.79 kJ/mol, respectively (Table 2). A study about iron recovery has been studied by Zhongyang et al. (2022) [12] reported that the reaction rate and activation energy were $1.09 \times 10^5/\text{min}$ and 50.68 kJ/mol, respectively, they were significantly lower than that of Zhongyang et al. (2022). Meanwhile, the apparent activation energy of the diffusion and chemical surface reaction-controlled models were generally less than 20 kJ/mol. Temperature was found to have little effect on activation energy, as evidenced by the low value obtained. Lastly, as the apparent activation energy of the mixed-controlled model exceeded 40 kJ/mol, the iron leached from the EAFS in a mixed-controlled process.

4.3 Cyclic voltammetry

Cyclic voltammetry (CV) is a well-known electrochemical method of measuring and defining the current profile of an electrochemical cell. During CV, a voltammogram is used to measure the electrical current of the electron transfer that occurs between the electrode and the active species, which results in the species being oxidised or reduced. Therefore, cyclic voltammetry was used to quantitatively and qualitatively investigate the electrochemical reactivity and electrode kinetics of the iron-screen-printed carbon electrode (Fe-SPCE). As seen in Figure 4, the applied potential imposed on the system was plotted along the x-axis while the response of the passing current was plotted along the y-axis. The tests were conducted within a potential range of -2-2 V and a scan rate of 100 mV/s with an SPCE. The CV redox peaks, which represent the reduction and oxidation peaks of the material, depicts the capacitive nature of the electrode. One oxidative peak can be observed at 0.7 and 0.6 V at 60 and 80 °C while two reduction peaks were observed at -0.9 and 0.9 V at 60 °C meanwhile 0.7 and -1 V at 80 °C, respectively. The maximum I_{pa} response was observed at 80 °C with a rate constant of 0.0005 min^{-1} . The differences between the I_{pa} responses at other temperature were insignificant. This could be due to their rate constants, which were between 0.0002 - 0.0006 min^{-1} . Figure 5 depicts the CVs at all the investigated temperatures. The oxidation peaks occurred when Fe^{2+} was oxidised to Fe^{3+} while sulphuric acid was being reduced.

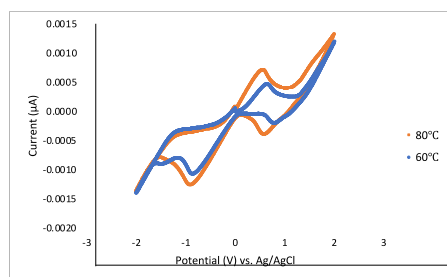


Figure 4: The CV of the iron-rich leaching solution at a scan rate of 1 mV/s with an SPCE and a 0.1 M sodium chloride

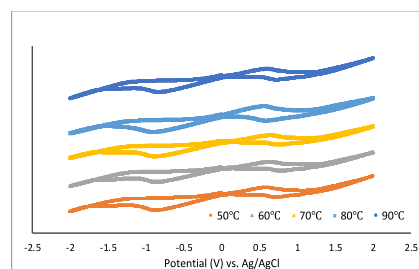


Figure 5: The CV of the iron-rich leaching solution at a scan rate of 1 mV/s with an SPCE and a 0.1 M sodium chloride

5 Conclusions

This present study evaluated the leaching kinetics of iron from EAFS in oxidative and non-oxidative leaching environments. The selective leaching of iron was found to follow the chemical reaction-controlled model with an activation energy of 16.9522 kJ/mol. This study was further corroborated by the results of a CV that showed two distinct oxidation and reduction peaks. However, future studies may investigate conducting CV at various scan rates to evaluate the reversibility of the electrochemical reactions of the active species on an SPCE for the potential elemental recovery of iron in solid form.

6 Declarations

6.1 Acknowledgements

The authors would like to acknowledge receiving financial support from the Ministry of Higher Education (MOHE) and Universiti Teknologi MARA (UiTM) under Fundamental Research Grant (FRGS) (FRGS/1/2019/TK02/UITM/02/5). The authors would also like to thank the College of Engineering, UiTM Shah Alam for providing the research facilities.

6.2 Funding source

Fundamental Research Grant (FRGS) (FRGS/1/2019/TK02/UITM/02/5).

6.3 Competing Interests

There is no conflict of interest exist

6.4 Publisher's Note

AJR remains neutral with regard to jurisdiction claims in published maps and institutional affiliations.

References

- [1] S. Monosi, M. L. Ruello, and D. Sani, "Electric arc furnace slag as natural aggregate replacement in concrete production," *Cement and Concrete Composites*, vol. 66, pp. 66-72, 2016, doi: 10.1016/j.cemconcomp.2015.10.004.
- [2] X. Lin et al., "Pyrometallurgical recycling of electric arc furnace dust," *Journal of Cleaner Production*, vol. 149, pp. 1079-1100, 2017, doi: 10.1016/j.jclepro.2017.02.128.
- [3] A. Bakkar, "Recycling of electric arc furnace dust through dissolution in deep eutectic ionic liquids and electrowinning," *J Hazard Mater*, vol. 280, pp. 191-9, Sep 15 2014, doi: 10.1016/j.jhazmat.2014.07.066.
- [4] X. Chen, B. Xu, T. Zhou, D. Liu, H. Hu, and S. Fan, "Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries," *Separation and Purification Technology*, vol. 144, pp. 197-205, 2015, doi: 10.1016/j.seppur.2015.02.006.
- [5] W. Gao et al., "Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries," *Waste Manag*, vol. 75, pp. 477-485, May 2018, doi: 10.1016/j.wasman.2018.02.023.
- [6] F. Faleschini, K. Brunelli, M. A. Zanini, M. Dabalà, and C. Pellegrino, "Electric Arc Furnace Slag as Coarse Recycled Aggregate for Concrete Production," *Journal of Sustainable Metallurgy*, vol. 2, no. 1, pp. 44-50, 2015, doi: 10.1007/s40831-015-0029-1.

- [7] I. Z. Yildirim and M. Prezzi, "Experimental evaluation of EAF ladle steel slag as a geo-fill material: Mineralogical, physical & mechanical properties," *Construction and Building Materials*, vol. 154, pp. 23-33, 2017, doi: 10.1016/j.conbuildmat.2017.07.149.
- [8] N. Nasuha, S. Ismail, and B. H. Hameed, "Activated electric arc furnace slag as an efficient and reusable heterogeneous Fenton-like catalyst for the degradation of Reactive Black 5," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 67, pp. 235-243, 2016, doi: 10.1016/j.jtice.2016.07.023.
- [9] P. T. Teo *et al.*, "Assessment of Electric Arc Furnace (EAF) Steel Slag Waste's Recycling Options into Value Added Green Products: A Review," *Metals*, vol. 10, no. 10, 2020, doi: 10.3390/met10101347.
- [10] N. Nasuha, S. Ismail, and B. H. Hameed, "Activated electric arc furnace slag as an effective and reusable Fenton-like catalyst for the photodegradation of methylene blue and acid blue 29," *J Environ Manage*, vol. 196, pp. 323-329, Jul 1 2017, doi: 10.1016/j.jenvman.2017.02.070.
- [11] J. Ait Brahim, S. Ait Hak, B. Achiou, R. Boulif, R. Beniazza, and R. Benhida, "Kinetics and mechanisms of leaching of rare earth elements from secondary resources," *Minerals Engineering*, vol. 177, 2022, doi: 10.1016/j.mineng.2021.107351.
- [12] Z. Lv, X. Pan, X. Geng, and H. Yu, "Synergistic removal of calcium and iron impurities from calcium-rich and high-alumina fly ash by acid leaching control," *Journal of Environmental Chemical Engineering*, vol. 10, no. 2, 2022, doi: 10.1016/j.jece.2022.107268.