

Carboxylic Acid-Assisted Leaching of Critical Elements from Coal Fly Ash: Experimental and Simulation Studies

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GRAPHICAL ABSTRACT

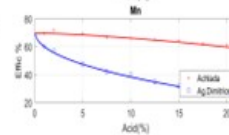
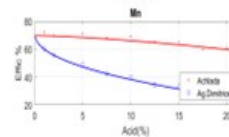
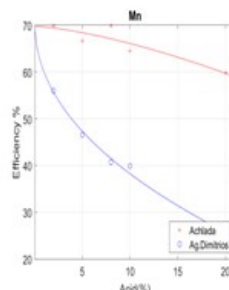
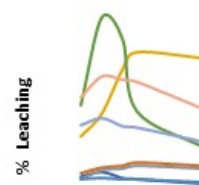
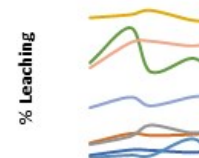
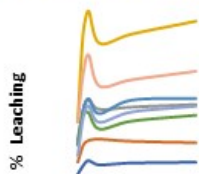
Leaching experiments Simulations



Leaching with
carboxylic acids



CRITICAL
METALS



$$\% L = a_0 + a_1 P_1 + a_2 P_2 + a_3 P_3$$

— Li — Ce — La — Cr — Ni — Zn — Co — Mn

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ABSTRACT

Critical elements are essential in a variety of high-tech applications. In the context of the circular economy, demand has arisen for technologies that are able to recover high-tech metals from wastes and byproducts. The aim of the present study is to investigate the leaching potential of critical elements from coal fly ash (CFA) using carboxylic acids as a milder yet efficient leaching agent. The leaching efficiency of citric acid and acetic acid was investigated in a simple single step process (pH 2.5-3.5 depending on the fly ash used) and the effect of acid type, acid concentration, temperature, and time on the process was studied with leaching experiments and the parameters were simulated using a non-linear equation and the uniform random distribution through MONTE CARLO simulations. Two coal fly ashes were studied. The major constituents of the fly ashes were analyzed by X-ray fluorescence spectroscopy (XRF) and their mineralogy was studied by X-ray powder diffraction (XRD). The content of fly ash samples in critical elements (Zn, Cr, Co, Mn, Ni, La, Ce, Li) as well as critical elements in the leachates, was determined by ICP–MS. The results revealed that citric acid appeared to be a better leaching agent, in most cases, with leaching efficiencies that reached 88%. The leaching efficiency for both acids in all cases was much higher for transition metals studied, compared to La, Ce, and Li. Experimental results adequately fitted to a non-linear equation in all cases with MARE < 11% and equations relating elements' recovery to the three parameters investigated were successfully (MARE<16%) produced.

Keywords: critical elements, fly ash, leaching, carboxylic acids, recovery, circular economy, simulation

1. Introduction

Critical elements have attracted significant attention, due to their increasing prevalence in various high-tech applications and the use of these elements in a wide range of products, including electronics, optics, magnets, and catalysts among others, has led to their increased demand. It is obvious that maintaining the supply of these elements is vital and, as the modern society is leaning towards cleaner and more sustainable mining activities, in the context of circular economy and industrial ecology, the research on critical elements recovery from secondary resources, is becoming increasingly important (Hageluken, 2022, Vilakazi, 2022). Given the importance of critical elements, in addition to actually evolving waste streams, wastes or byproducts which have been produced throughout the years and deposited in the past, can be utilised as secondary resources and be considered as anthropogenic “ore deposits”, which can be handled similarly to primary raw materials. Such secondary can be found in landfills, mining residues, slags, and ashes dumps from smelters and incineration or power generation plants. Lately, several researchers (Bhatt, 2019, Dai, 2018, Dai and Finkelman, 2018, Finkelman, 2019, Hu, 2018, Marinakis, 2020, Qin, 2015, Sahoo, 2016, Seredin, 2012, Talan, 2022, Talan and Huang, 2022, Zhang, 2020, Zhou, 2022) have proposed coal, coal-bearing formations and coal combustion byproducts as an alternative source of critical elements, including Zn, Cr, Mn, Ni, La, Ce, and Li, in the transition to a “green” economy. Despite commitments and efforts to develop sustainable energy sources, coal is still widely used for energy generation and coal-fired power plants, are estimated to generate 1 billion tons of coal ash every year (Talan and Huang, 2022, Vilakazi, 2022, Zhang, 2020) with China to produce 500 million tons annually. Coal fly ash belongs to the industry byproducts that possess alarming environmental concern and extensive research studies are carried out around the world, in order to explore the potential of its effective utilization (Sahoo, 2016, Vilakazi, 2022, Zhao, 2019, Zou, 2020, Zhang and Honaker, 2020). Statistics on coal fly ash commercialization varies between countries. Countries in Europe (Denmark and Italy recycle 100% of the total production) as well as USA have high utilization rates while about 10% is re purposed in countries like China and South Africa (Vilakazi, 2022). Research on fly ash eco-friendly utilization

is expanding into various fields and a number of applications have been proposed aiming to recycle or repurpose it. For instance, such applications include production of various materials such as zeolites, fertilizers, construction materials, fillers, polymers and ceramics. It is estimated (Rezaei, 2022) however, that only 25% of the fly ash produced is utilized and huge unutilized quantities are treated by stockpiling, a practice that arises environmental concerns. Consequently, critical metal recovery from CFA, in the context of circular economy, has attracted the interest of scientific community and is of major importance, since it not only promotes waste valorisation but also contributes to the conservation of natural resources.

Recovering critical elements from CFA heavily depends on hydrometallurgy using either direct inorganic leaching, leaching with more “green” ionic liquids or deep eutectic solvents, or roasting followed by mineral acids leaching. Some researchers have suggested preconcentration of critical elements based on physical separation and methods applied to enrich metals in various minerals or ores. To address certain concerns and limitation that come along with reagents employed by the above-mentioned procedures, some carboxylic acids have been proposed lately, as alternative leaching agents which are easily available, less corrosive, bound to have a lower environmental impact during and after the leaching process (Manurung, 2020, Prihutami, 2020, Banerjee R., 2021, Prihutami, 2021, Banerjee R., 2022, Rezaei H. 2022).

In the present study, with the aim to contribute to promoting waste valorisation, the leaching potential of five transition metals (Zn, Co, Cr, Mn, Ni), La, Ce as representative of light rare earth elements (LREE) and Li, from two coal fly ash samples, in a single step process using carboxylic acids is investigated. The fly ashes studied were of different type (class F and C), and acetic acid and citric acid were used as the leaching agents. The effect of acid type, leaching duration, temperature, and carboxylic acid concentration on the leaching efficiency was studied. In addition, with the aim to further analyze experimental results and have reliable predictions of the effect of the tested variables, the main parameters were simulated using a non-linear equation and the uniform random distribution

through MONTE CARLO simulations. The simulations were produced using original code in the Matlab 2023a software.

2. Experimental section

2.1. MATERIALS AND METHODS

Two fly ash samples, namely Achlada (ACH) and Ag. Demetrios (AGD), from thermal power plants located in northern Greece were studied. The samples, collected from the corresponding precipitators, were air dried at room temperature for 24 h and subsequently oven dried at 105 °C overnight prior of being used for characterization analyses and leaching experiments. The samples underwent no crushing and were used without further conditioning or treatment. All reagents used for analyses and leaching experiments were of analytical quality, purchased from Sigma Aldrich, Steinheim (Germany). Based on literature performing leaching experiments in duplicate was considered sufficient. Reported values are the corresponding mean values of experimental results that were less than 0,05 mg/kg apart.

2.2. SAMPLES CHARACTERIZATION

The mineral constituents of the samples were studied by powder X-ray diffraction (XRD) using the D8-Advance diffractometer by Bruker AXS with a Cu X-ray tube and LynxEye detector with a Ni filter. The patterns were recorded in a 2-theta (2θ) range from 2 to 70°, in steps of 0.02°, and the counting time was 0.4 s per step. Corundum was used as an internal standard for semi-quantitative analysis. Diffrac_{plus} EVA by Bruker AXS and Seifert Autoquan software were employed for qualitative and semi-quantitative analysis, respectively.

The major constituents of the samples (flux beads with lithium metaborate) were analyzed by X-ray fluorescence spectroscopy (XRF) using the S2 Ranger V5 analyzer by Bruker, equipped with a Pd anode X-ray tube and a silicon drift detector. Prior to XRF analysis, the samples were burned at 950 °C in a muffle furnace until constant weight was achieved and loss on ignition (LOI) was calculated.

The content of the elements Zn, Cr, Co, Mn, Ni, La, Ce, Li of the samples was determined by inductively coupled plasma mass spectrometry (ICP–MS) after total dissolution by acid digestion. For the analyses, the NexION 2000 ICP–MS system by Perkin Elper was employed. The results, reported in mg/Kg, are produced using the appropriate calculations, taking into account the sample dissolution process (0.25 g sample to 50 mL solution).

2.3 LEACHING EXPERIMENTS

Acetic acid and citric acid were employed as leaching agents for the leaching experiments. In a typical experiment 0.5g of fly ash was transferred in a PTFE container and 50 mL of aqueous organic acid solution was added to it. The container was closed and stirred at 600rpm at a desired temperature for a specific period using a hotplate cum magnetic stirrer. The residual ash was separated from the leaching solution by filtering with Whatman 42 filter paper and concentration of elements of interest in the clear leaching solution, after acidification with HNO₃, were measured using ICP-MS. The effect of leaching duration, temperature, and carboxylic acid concentration on the process and leaching efficiency was investigated by performing three sets of experiments varying the parameters investigated as described on Table 1 where characters in bold indicate the values that were kept constant in each set of experiments. Leaching duration varied between 12 and 120 hours and temperature and carboxylic acid concentration ranged between 40 - 90°C, and 2 – 20 % respectively. No pH adjustments were made. Initial pH and pH throughout the experiments were monitored using a pHmeter (model InolabLevel1, by WTW). pH fluctuated throughout the experiments, for both carboxylic acids, around 2.5 and 3.5 for Achlada and Ag. Demetrios fly ash samples respectively.

2.4. SIMULATIONS

As described above, in each set of experiments, two parameters were kept constant while the third one was systematically varied (Table 1) in order to isolate and study the effect that the certain parameter had on the leaching process. The experimental results were further studied by conducting 100 different simulations for each of the tested parameters (acid concentration, leaching duration, temperature) and both acids used as the leaching agent. The aim was to extend and expand the analysis

beyond the values tested by the leaching experiments and get reliable prediction of the effect of the parameters tested, in line with and guided by the experimental results, without the cost and time that would be required by such extensive testing.

Using the % leaching efficiency and the corresponding tested values of the varying parameter, a trend line (Hristopoulos, 2020) was fitted for each acid. The trend line was of the form

$$R = a P^n + b, \quad (\text{Eq.1})$$

where R is the % leaching efficiency of the element, P is the parameter being tested (leaching duration, temperature, acid concentration). The coefficients a , b and n were the ones that resulted in the best fit. The way to determine the best fit was to numerically calculate the values of coefficients a , b and n that minimize the square error of the trend line (Eq.1) and the experimental results (Hristopoulos, 2020).

Following the estimation of the trend line for each element and each acid for each of the parameters, analysis was extended by conducting simulations to predict % leaching efficiency beyond the original experimental conditions using the Monte Carlo method described in Metropolis, 2009.

For each experimental configuration, 100 simulations, independent from one another, were conducted. The estimated value for % leaching efficiency was in each case calculated from Eq.1. Then, the prediction of each simulation was adjusted by an error. The range of the error was set as the observed error range from the experiments. For example, if the error range of R for Temperature was between -0.3 mg/kg and 0.5 mg/kg, then the error integrated to each simulation at each predicted point was randomly taken between -0.3 mg/kg and 0.5 mg/kg.

In order to validate the simulation results the residual errors between the predicted values \hat{R}_i and the observed values R_i for the tested parameter P_i was calculated. Since the % leaching recoveries of different elements for the two samples, vary significantly, we decided to use a modification variation of the Mean Absolute Relative Error (MARE), shown in Eq.2.

$$MARE = \sum_{i=1}^N \frac{\hat{R}_i - R_i}{R_i} \quad (\text{Eq.2})$$

Unlike the usual definition of MARE, we decided to use the mean value \bar{R}_i to standardize the error metric (Chiles, 2012).

Using MARE, the results of the simulations for the different elements, acid type, investigated parameter and fly ash sample could be adequately compared.

Similar to finding a trend line for R by changing a single parameter each time and keeping the others constant, a linear trend line was fit to the data by simultaneously taking into account all three variables.

$$R = a_0 + a_1 P_1 + a_2 P_2 + a_3 P_3, \quad (\text{Eq.3})$$

where P_1, P_2, P_3 are the variables (leaching duration, temperature, acid concentration) and a_0, a_1, a_2, a_3 are the coefficients. The values of the coefficient were estimated by using multilinear regression (Chiles, 2012).

3. Results and Discussion

3.1. SAMPLE CHARACTERIZATION

The results (semi quantitative analysis) of the mineralogy of the samples are illustrated in Table 2 and Figure 1. Amorphous material, represented by a broad peak (amorphous hump) at lower angles $\sim 10^\circ$, is the most abundant constituent for both samples, with a content of 33 % and 63 % for AGD and ACH samples respectively. This is a result in accordance with the literature (Auhengebaur, 2016, Adamidou, 2007, Filippidis, 1992, Koukouzas, 2010, Zou, 2021) where fly ashes are reported to contain significant amounts of amorphous glassy material. The two fly ashes possess different mineralogy with the main mineral phases that are encountered to be calcite (12 %), quartz (12 %), and anhydrite (10 %) for AGD and feldspars (11 %), mullite (10 %), and quartz (9 %) for ACH. It is worth noticing that only the ACH sample appeared to contain mullite, a mineral typical for high-alumina fly ashes that could be associated with elevated REE and Li contents (Ward, 2016, Ward, 1999, Dai, 2020).

The results of the major elements analysis, expressed as weight percent (wt %) of metal oxides, are illustrated in Table 3. The major element analysis is, as expected, in accordance with the mineralogical analysis. The elements silicon and calcium appear to be the major components for AGD sample, while silicon and aluminum appear to be the major components for ACH sample. Due to its low CaO and high aluminosilicate content, the ACH sample is classified as class F while AGD sample with a relatively high calcium content is classified as class C (Filippidis, 1996, Finkelman, 1993). The contents of the elements Zn, Cr, Co, Mn, Ni, La, Ce, and Li, are reported in Table 4 and the elements Li, Ce, Co, Cr, Ni, Mn and Zn can be considered enriched compared to CFA worldwide (Kertis and Yudovich, 2009) with enrichment factors >1.

3.2. LEACHING EXPERIMENTS

The leaching efficiency was calculated based on the equation:

$$L = \frac{a * V * 100}{A * m}$$

where a denotes the metal concentration (in mg/L) in the leachates, V the volume (in mL) of the leaching solution, A is the metal concentration (in mg/kg) of the fly ash sample, and m (in g) represents the mass of the sample used for the leaching experiments. The highest % leaching efficiencies, for both leaching agents used and corresponding experimental parameters, are reported in Figure 2 and 3 for AGD and ACH samples respectively. The results of the leaching experiments reveal that for the elements studied and for both fly ash samples, citric acid appears to be a more efficient leaching agent. Exception to this trend, as is depicted in Figure 2 and 3, is observed for Cr, Ni, and Zn, in the case of ACH sample, where acetic acid proved to be more efficient leaching agent. It is also observed that the leaching efficiency for both acids in all cases was much higher (up to 88%) for transition elements compared to La and Ce (up to 35%) and Li (up to 15%). Exception to this trend is observed for Ni in the case of ACH sample where leaching efficiency is lower than 15%. Such observations are in accordance with literature (Prihutami, 2020, Banerjee R., 2021, Prihutami, 2021, Banerjee R., 2022) and could be explained based on the specific conditions and corresponding mechanism of complexation as well as the mode of occurrence of the elements in the sample matrix. The citric acid,

for example being a stronger acid (higher K_{a1}) and tridentate chelating agent with one hydroxyl group, is expected and is reported to be better than acetic acid as leaching/complexing agent, but in certain cases, in our study as well as elsewhere (Banerjee, 2021, Prihutami, 2021) unexpected leaching behavior is observed for specific elements and organic acids. Unexpected leaching behavior could be attributed to the type and corresponding stability constant values of complexes or precipitates and corresponding solubility products, that are expected to form in the specific leaching conditions. Work is in progress to study morphology and mineralogy of the experiments' residue, to attain a better insight to the complex chemical transformations which take place throughout the experiments.

3.2.1. EFFECT OF ACID CONCENTRATION

The effect of acid concentration to leaching efficiency is reported in Figure 4 and Figure 5 for AGD and ACH sample respectively. Differences are observed for the different samples. In the case of AGD samples the effect of acid concentration to leaching efficiency depends on acid type. A uniform trend is observed for citric acid for all elements studied where increase in acid concentration results in decrease in % leaching efficiency. A less uniform trend is observed when acetic acid is used, with a relatively sharp increase in % leaching efficiency as acid concentration increases with a maximum at 5% or 10% acetic acid for Co, Cr, Mn, Ce or Ni, La, Zn, Li respectively and no influence for Li. It should be noted here that % leaching efficiency of acetic acid was low, no higher than 13%. In the case of ACH sample, the leaching efficiency, appears to be affected differently depended on the element studied. For elements Li, Ni, Ce, La, and Co no significant influence of acid concentration on leaching was observed, while for the elements Mn, and Zn the maximum leaching efficiency is observed for acid concentrations between 5 and 10%. Leaching of Cr, on the other hand, when citric acid was used as the leaching agent, increased linearly with the acid concentration increase.

3.2.2 EFFECT OF TIME

The effect of leaching duration to leaching efficiency is reported in Figure 6 and Figure 7 for AGD and ACH sample respectively. The influence of time to the leaching process is different for the two

fly ash samples. In the case of AGD sample a rather uniform influence is observed for all elements and both leaching agents. The % leaching efficiency appears to sharply increase until about 0.3 h, to decrease slightly until 0.5 h and remain practically constant after 0.5 h. In this case again, % leaching efficiency of acetic acid was low, no higher than 15%. In the case of ACH sample again, the leaching efficiency, appears to be affected differently depended on the acid type used and the element studied. The leaching efficiency of citric acid appears to gradually increase with increasing leaching duration reaching a maximum at 1 hour. Exception to this trend is observed for elements Cr and Ni where no influence is observed. On the other hand, no significant influence of time, on acetic acid leaching efficiency is observed with the exception of Zn where a maximum is observed at 1 hour.

3.2.3 EFFECT OF TEMPERATURE

The effect of temperature to leaching efficiency is reported in Figure 8 and Figure 9 for AGD and ACH sample respectively. Temperature too appears to affect leaching efficiency differently for the two samples studied. In the case of AGD sample, with the exception of Li, where no significant influence is observed, and Zn when acetic acid is used, a maximum of leaching efficiency is observed for both acids at 60°C. In the case of ACH on the other hand, no significant effect of temperature, on leaching efficiency of both acids is observed, with the exception of Zn where leaching efficiency of acetic acid appears to sharply increase after 80°C and leaching efficiency of acetic acid reaches a maximum at 50°C.

3.3. SIMULATIONS

As mentioned, 100 different simulations for each of the leaching experiments were conducted in order to extend and expand the analysis beyond the values tested by the experiments. The variation of the simulated % leaching efficiency from the model equation for the parameters studied, is in line with the experimental observations. The error metric MARE, described in Eq.2, which was used to validate the results, was 8.4% and 11.0% for the ACH and AGD samples respectively, implying that the predictions can be considered adequate. In Figure 10, an example of the fit of equation 1 is reported (for Mn recovery as a function of acid concentration in the case of AGD sample). In the same figure

the results from two of the 100 simulations conducted are showcased. The trend line of Eq.1 was an adequate fit to the experimental values (MARE = 6.9%).

The linear trend line that takes into account all three variables to predict the leaching efficiency (Eq.3) performs well in all cases, having strong correlation to data ($\rho > 50\%$) (Goovaerts, 1997) and MARE $< 16.1\%$. Generally, Eq.3 gives the best fit for Lithium data ($\rho = 95.8\%$, MARE = 5.6%) and the worst fit for Zn ($\rho = 52.3\%$, MARE = 16.1%). As a result, the simulation of the non-linear trend lines gives simulations that capture the variation of the observed results. Non-linear trend lines for individual parameters and a multilinear trend line were fit on the error metrics (like MARE) and give an adequate fit. Coefficient a_0 is the intercept of the regression model. Theoretically it is the predicted value for the recovery if all independent parameters were zero which is practically impossible. Thus, a_0 is a mathematical construct that helps us understand the relative contributions of the Temperature, concentration and duration to the predicted leaching recovery. By conducting 100 Monte Carlo simulations for each parameter and for each sample the findings were extended and it was possible to estimate the impact of varying conditions without incurring additional time and cost.

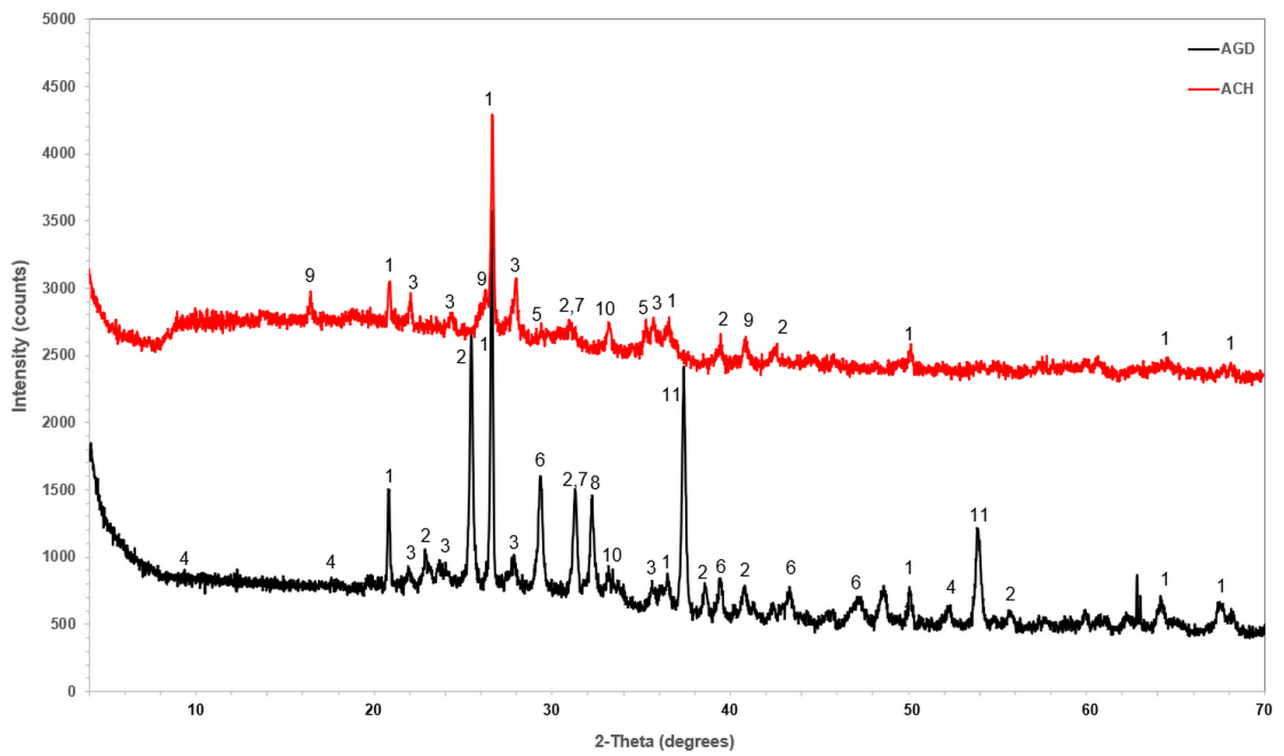
In Table 5 and 6, as an example, the coefficients for the linear trend and the validation measures respectively, are reported for Mn leaching by citric acid, in the case of ACH sample and La leaching by the same acid for AGD sample.

4. Conclusions

The results of the leaching experiments performed using citric acid and acetic acid, with the aim to contribute to attaining insight in the complex leaching process of critical elements from two CFA of different type, revealed that the influence of the parameters studied to the leaching process varies depending on fly ash sample, acid type and element examined. This can be explained based on the specific conditions and corresponding mechanism of complexation as well as the mode of occurrence

of the elements in the sample matrix. In most cases citric acid appears to be a better leaching agent compared to acetic acid. Leaching efficiency for both acids in all cases was much higher (up to 88%) for transition elements studied compared to LREE La and Ce (up to 35%) and Li (up to 15%). Both the non-linear and linear trend lines present an adequate fit, based on the error metrics (like MARE and correlation coefficient). Those trend lines were used to create simulations that capture well the variation of the observed results. The use of simulations in this study enhances the reliability of predictions of the leaching efficiency beyond the experimental conditions. Our study suggests that Monte Carlo simulations can be effectively applied in similar studies to optimize experimental designs while avoiding the costs and time required for an extensive number of experiments.

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1: Quartz, 2: Anhydrite, 3: Feldspar, 4: Mica, 5: Pyroxene, 6: Calcite, 7: Gehlenite, 8: C2S, 9: Mullite, 10: Hematite, 11: Lime

Figure 1. Samples mineralogy

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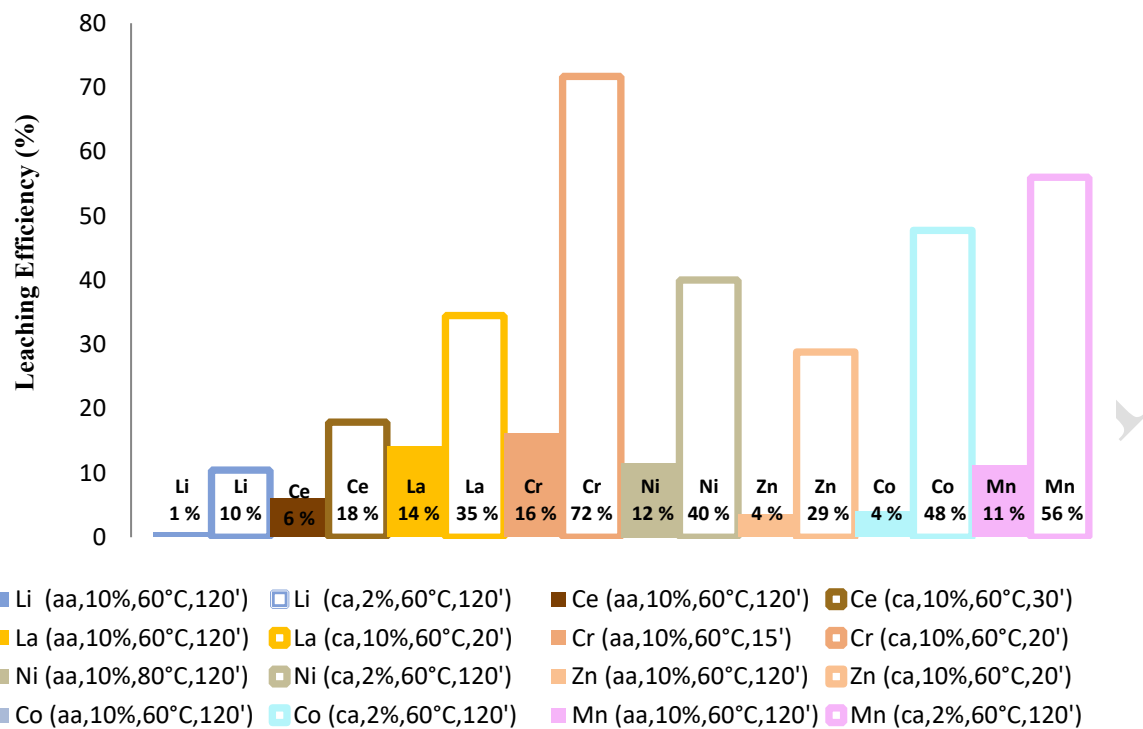


Figure 2. The highest % leaching efficiencies, for citric acid (ca) and acetic acid (aa) and corresponding experimental parameters, for each individual element studied in the case of AGD fly ash.

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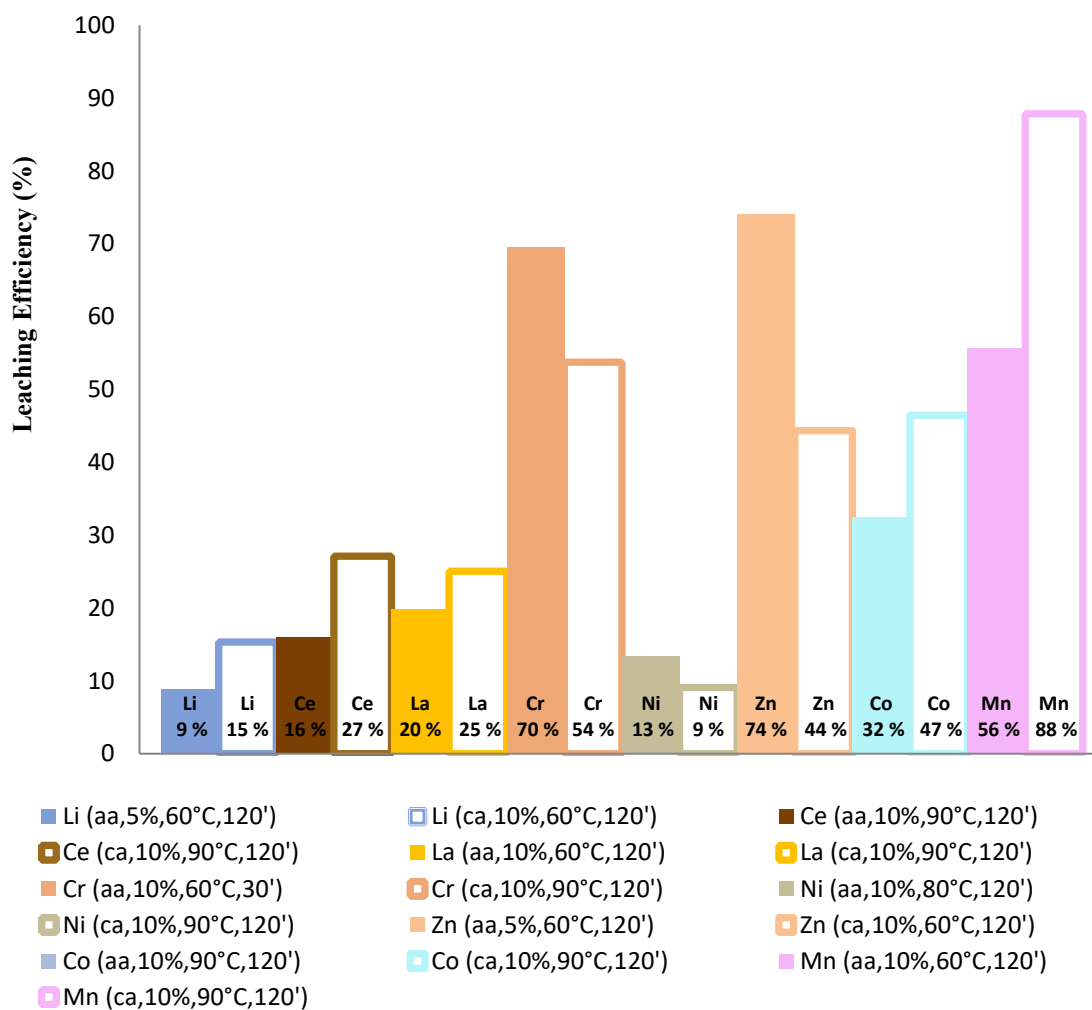


Figure 3. The highest % leaching efficiencies, for citric acid (ca) and acetic acid (aa) and corresponding experimental parameters, for each individual element studied in the case of ACH fly ash.

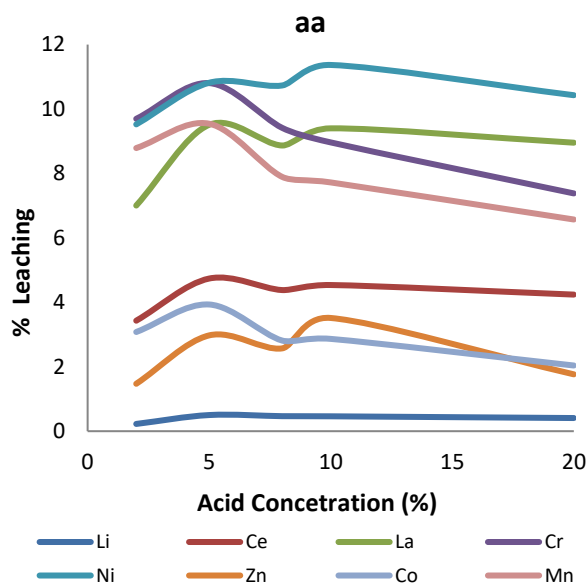
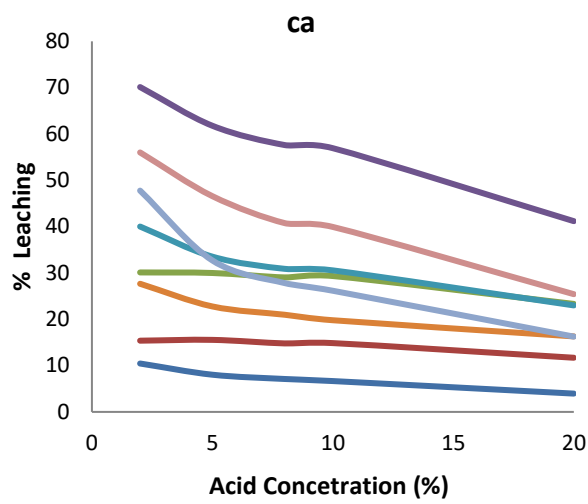


Figure 4. The effect of acid concentration on leaching efficiency of citric acid (ca) and acetic acid (aa) for AGD fly ash. (solid to liquid ratio: 0.5g/50 mL, temperature: 60 °C, time:2 h)

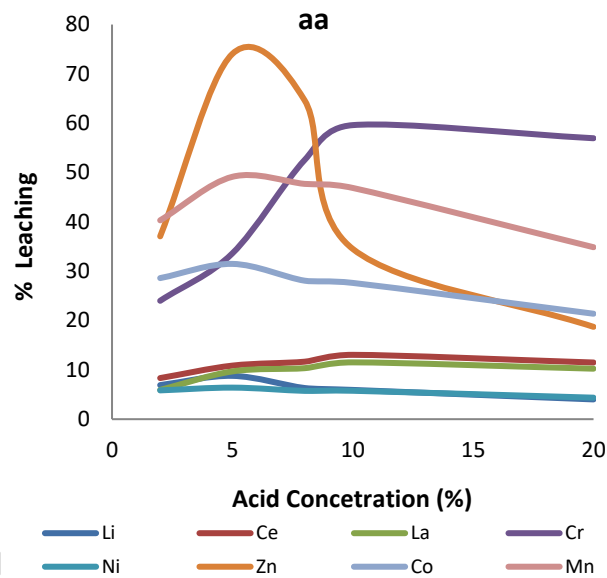
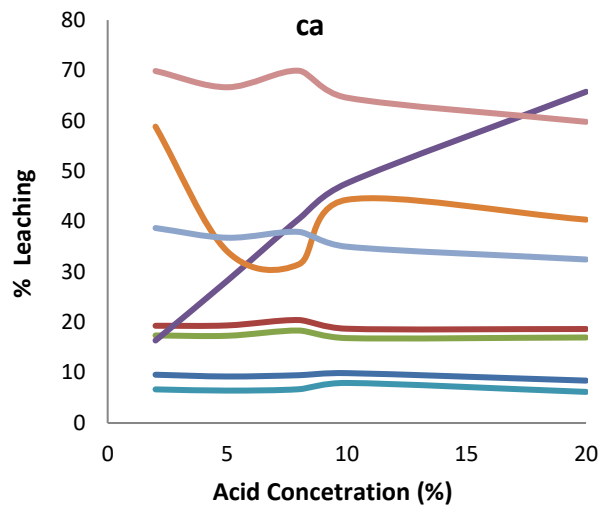


Figure 5. The effect of acid concentration on leaching efficiency of citric acid (ca) and acetic acid (aa) for ACH fly ash. (solid to liquid ratio: 0.5g/50 mL, temperature: 60 °C, time:2 h)

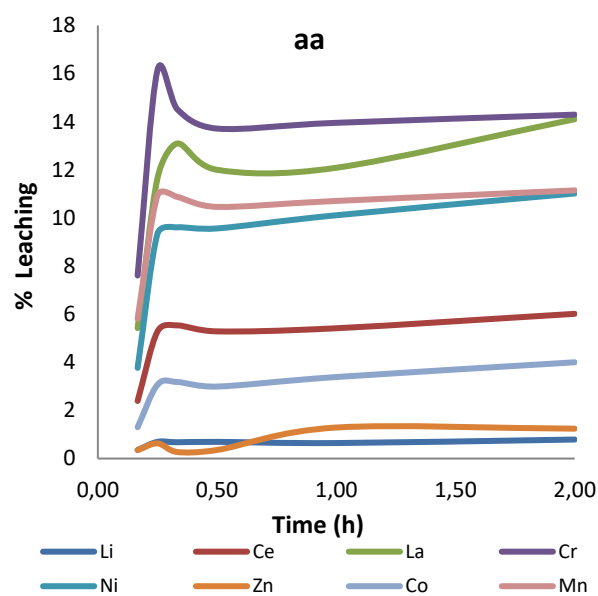
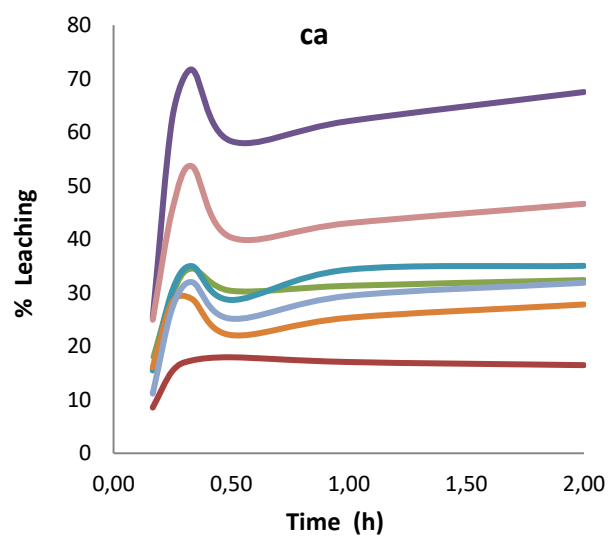


Figure 6. The effect of time on leaching efficiency of citric acid (ca) and acetic acid (aa) for AGD fly ash. (solid to liquid ratio: 0.5g/50 mL, temperature: 60 °C, acid concentration:10 %)

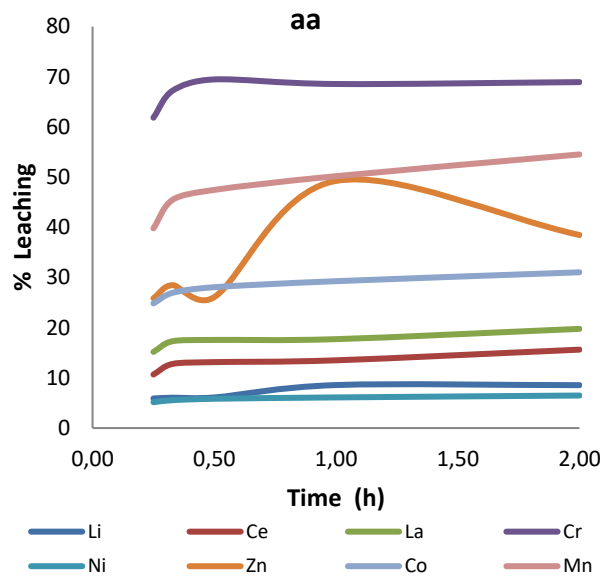
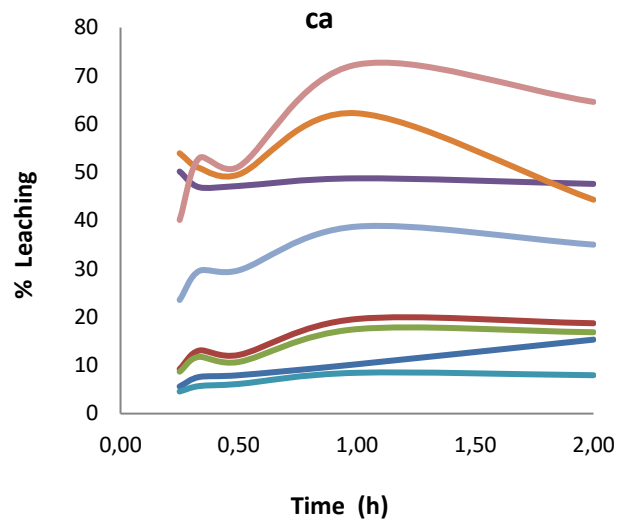


Figure 7. The effect of time on leaching efficiency of citric acid (ca) and acetic acid (aa) for ACH fly ash. (solid to liquid ratio: 0.5g/50 mL, temperature: 60 °C, acid concentration:10 %)

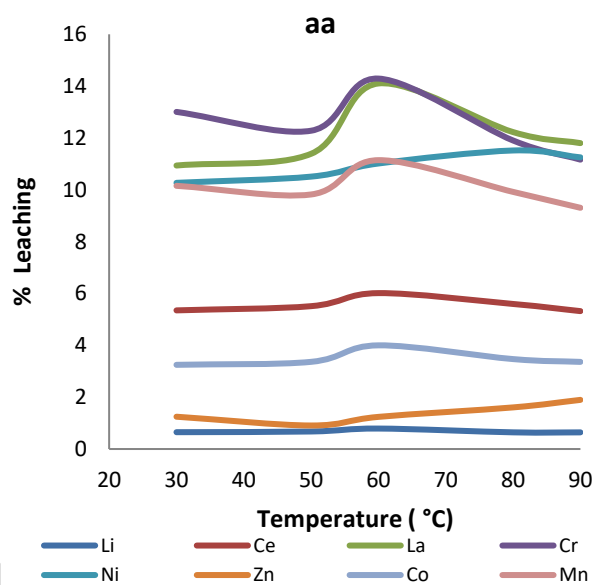
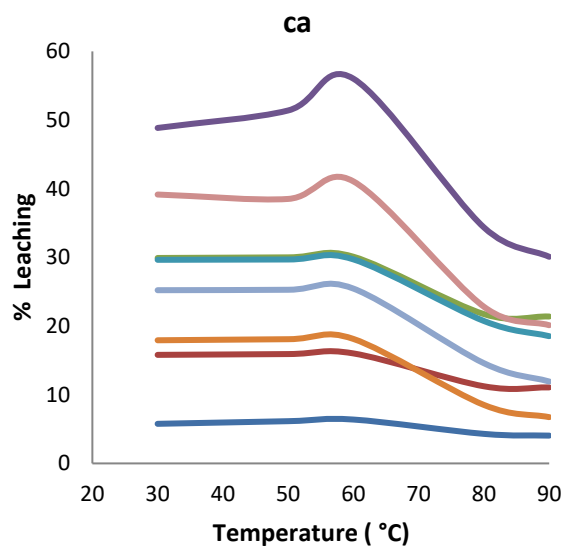


Figure 8. The effect of temperature on leaching efficiency of citric acid (ca) and acetic acid (aa) for AGD fly ash. (solid to liquid ratio: 0.5 g/50 mL, time: 2 h, acid concentration:10 %)

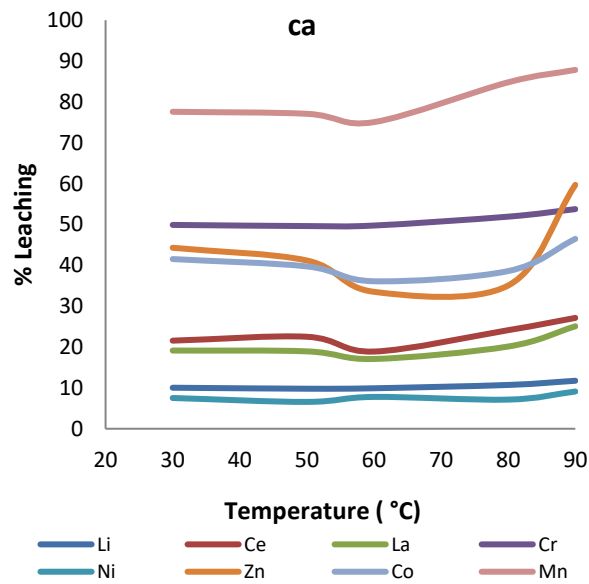
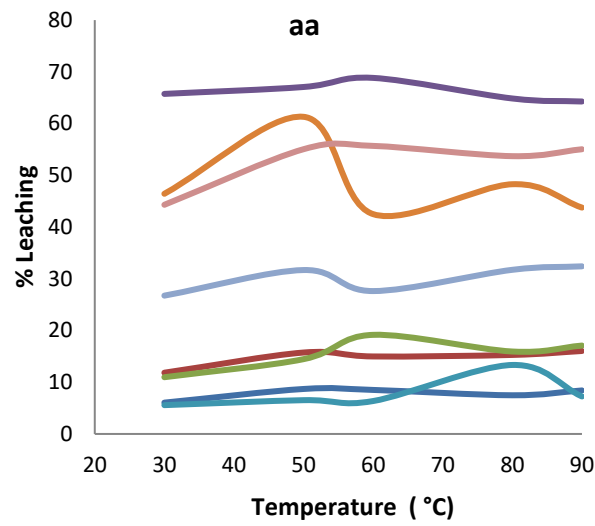


Figure 9. The effect of temperature on leaching efficiency of citric acid (ca) and acetic acid (aa) for ACH fly ash. (solid to liquid ratio: 0.5g/50 mL, time: 2 h, acid concentration:10%)

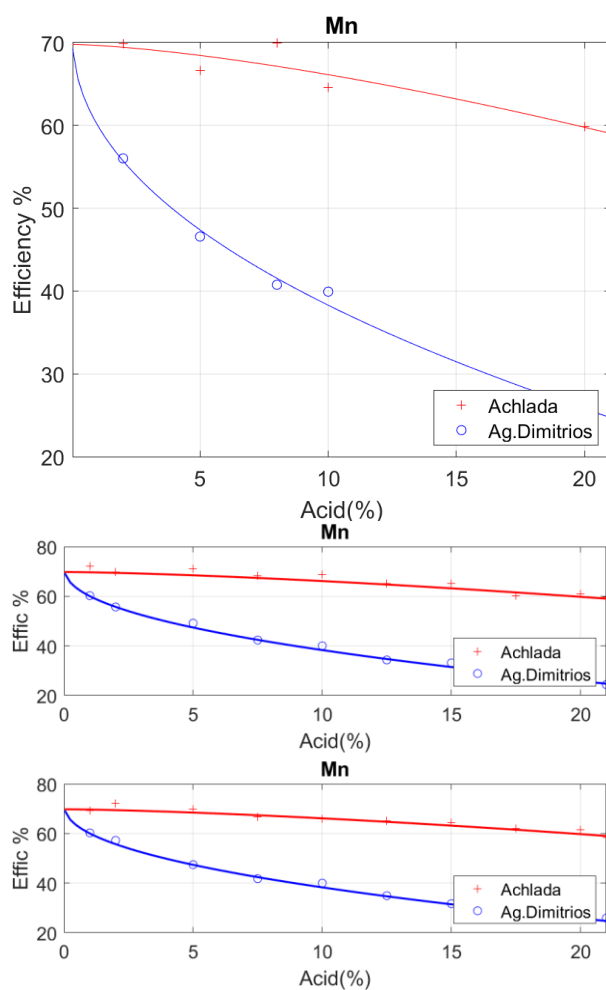


Figure 10. Trend Line of Eq.1 for Mn, as a function of citric acid concentration and corresponding simulation results. The fitting error in terms of MARE is equal to 6.9%.

Table 1 Experimental conditions. With bold characters the values kept constant are depicted.

Acid Concentration (%)				
2	5	8	10	20
Temperature (°C)				
30	50	60	80	90
Time (h)				
0.2	0.3	0.5	1.0	2.0

Table 2. Mineral and amorphous content in coal ashes (% semi-quantitative).

Mineral Phase	AGD	ACH
Anhydrite (CaSO ₄)	10	1
Hematite (Fe ₂ O ₃)	1	1
Calcite (CaCO ₃)	12	-
Portlandite [Ca(OH) ₂]	1	-
Lime (CaO)	9	-
Gehlenite [Ca ₂ Al(AlSiO ₇)]	4	-
C2S (Ca ₂ SiO ₄)	3	-
Brownmillerite (Ca ₂ (Al,Fe) ₂ O ₅)	4	-
Feldspar [(Ca,Na)Al ₁₋₂ Si ₂₋₃ O ₈ -KAlSi ₃ O ₈]	6	11
Quartz (SiO ₂)	12	8
Mica [KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂]	4	1
Pyroxene [(Ca,Mg,Fe,Al)Si ₂ O ₆]	1	2
Spinel (MgAl ₂ O ₄)	-	3
Mullite (Al ₆ Si ₂ O ₁₃)	-	10
Amorphous	33	63

Table 3. The major elements (as oxides %) and corresponding loss on ignition (LOI) for the studied fly ash samples.

Major Elements	AGD	ACH
Na ₂ O	0.2	0.2
CaO	30.8	5.3
Al ₂ O ₃	13.8	25.3
Fe ₂ O ₃	5.3	9.5
SiO ₂	36.6	49.2
MgO	4.1	3.7
K ₂ O	1.1	2.6
TiO ₂	0.8	0.9
P ₂ O ₅	0.1	0.1
SO ₃	7.1	2.6
LOI	0.1	0.5
SUM	100	100

Table 4. The critical elements contents (mg/Kg) for the studied fly ash samples.

Critical Element	AGD	ACH
Li	126	251
La	44	151
Ce	81	79
Cr	285	148
Ni	229	215
Zn	58	50
Co	17	15
Mn	384	389

Table 5. Coefficients for two elements, Mn and La.

Coefficient	Mn, ACH	La, AGD
a_0	43.06	33.579
a_1	14.235	3.033
a_2	-0.59625	-0.35103
a_3	0.41729	-0.11663

Table 6. Validation measures for two elements, Mn and La.

Error Metric	Mn, ACH	La, AGD
RMSE (%)	6.84	3.56
MARE (%)	7.1	9.7
ρ %	83.4	58.6

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