

Article

Lithium in Greek Coal Fly Ashes: Contents and Characterization by Sequential Extraction

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Abstract: Lithium belongs to the critical elements and is used 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. To achieve efficient recovery, apart from assessing metal enrichment, extensive knowledge of metal binding and leaching characteristics is required. The aim of the present study is to investigate the Li contents and mode of occurrence in Greek coal fly ashes. Eight coal fly ashes from different power plants in Greece were collected, and their major constituents were analyzed by X-ray fluorescence spectroscopy (XRF); their mineralogy was studied by X-ray powder diffraction (XRD), and their Li content was determined by ICP-MS. To identify Li binding and leaching characteristics, two sequential extraction methods (Tessier and BCR) were employed. The results showed that the Li content in the samples studied was between 95 and 256 µg/g and could be mainly attributed to the amorphous material encountered in the samples. The sequential extraction experiments revealed that 70–90% of Li is included in the residual fraction, indicating that it is strongly bound to the fly ash matrix.

Keywords: lithium; coal fly ash; circular economy; sequential extractions; secondary resource; recovery



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1. Introduction

The objective of the current study is to investigate the lithium (Li) content, enrichment, and binding and leaching characteristics in Greek fly ashes. This investigation aims to contribute to developing efficient Li recovery technology, with the ultimate goal of providing insights into the potential of using fly ashes as a secondary resource of lithium, a potential with a two-fold benefit, as it promotes both sustainability and environmental protection, in the context of a circular economy and industrial ecology.

The critical elements, including lithium, have attracted significant attention in recent years due to their increasing prevalence in various high-tech applications. 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 the circular economy and industrial ecology, research work is focused on secondary resource exploitation [1]. In addition to evolving waste streams, wastes or byproducts that have been produced throughout the years and deposited in the past can be considered anthropogenic “ore deposits” found in landfills, mining residues, slags, and ashes dumps from smelters and incineration or power generation plants. These wastes or byproducts can be used as secondary raw materials, which can be handled similarly to primary raw materials.

Lithium is a light and reactive metal that has a wide range of applications in different fields and industries. It is one of the critical elements that are essential for the development of modern technologies and the transition to a low-carbon economy. Even though lithium cannot be considered a rare element, it has been identified as a critical element (Minerals

Education Coalition, 2022). One of the main drivers of lithium demand is the rapidly increasing lithium-ion battery (LIB) industry. Lithium-ion batteries offer a high energy density, long cycle life, and environmental benefits compared to other types of batteries and are the preferred choice for electric vehicles and mobile phones. Despite the availability of several alternatives, such as hydrogen fuel cells, redox flow batteries, and solar panels, these substitutes often depend on different forms of lithium, which can be a limiting factor. Furthermore, another issue with such substitutions is performance, which is inferior in most cases. For instance, a lithium battery is capable of providing a significantly higher range than a solar-powered battery when used in a vehicle. Lithium is also used, as a key component, in the production of various alloys with metals such as aluminum, silicon, calcium, copper, magnesium, copper, bismuth and tin to enhance their properties for the purposes of the aerospace industry. It worth noting that the price of battery-grade lithium (Li_2CO_3) grew by a 162% increase in four years (2015–2018) and a 293% increase in the last two years (2021–2022) [2]. This trend is expected to continue in the foreseeable future with some experts predicting a worldwide lithium shortage as early as 2025. The increasing demand for lithium-ion batteries worldwide has led to a significant surge in the demand for lithium and due to lithium's unique properties and extensive use, its demand is forecast to quadruple in the next few years. This trend is expected to continue in the foreseeable future, as our society transitions towards a more sustainable and eco-friendly energy system [3]. The primary economic sources of lithium are brines, salt lakes, and pegmatite deposits, which are found in various parts of the world. In the last decade, Australia has emerged as the largest producer of lithium, exporting spodumene, a mineral from which lithium can be derived. However, more than 73% of the world's lithium resources are reported to be distributed in North and South America, with only a relatively small fraction (7%) found in Europe. Bolivia, located in the Lithium Triangle, is home to extensive lithium resources, including the world's largest single lithium deposit, the Salar de Uyuni salt flat. The rest of the lithium produced comes from Zimbabwe, Portugal, Argentina, and Chile, with a few other countries contributing smaller amounts [4].

Given the importance of the element in the context of a circular economy, research on lithium recovery from secondary resources is becoming increasingly important. Lately, several researchers [5–12] have proposed coal, coal-bearing formations and coal combustion byproducts as an alternative source of lithium in the transition to a green economy.

It is well known that coal as a naturally occurring substance has a complex and diverse formation history. Due to its origin, coal is expected to contain almost all elements of the periodic table [10,12]. It is well documented that the metallogensis of critical metals is influenced by a variety of geological processes and factors, including hydrothermal fluids, the contribution of terrigenous detrital materials, volcanic ash, seawater, and groundwater. These contributors can act jointly or separately and represent the processes responsible for deposit formation, which have a significant impact on the concentration, the distribution and the mode of occurrence of the elements in the coal matrix. Consequently, elements, including Li, encountered in coal can be either organic or inorganic-associated but can also exhibit mixed organic–inorganic affinity [4,13–19].

Several researchers [16,19–21] have reported that Li appears to be enriched in coal and coal combustion byproducts and can reach the degree and scale of industrial utilization. In particular, coal fly ash has attracted interest as a promising secondary resource for Li [5,7,11,17,18,21]. Greek lignites and corresponding ashes are reported to exhibit elevated contents in critical elements [9,22–25], and their utilization as secondary raw materials is increasingly discussed [9] as part of the trend that has been observed across the world in recent years. Coal fly ash is the major component of coal combustion byproducts, and since the world's power generation is still strongly dependent on coal-firing, 1 billion tons of coal ash is estimated to be produced every year [6,16,26,27]. China produces 500 million tons annually, while according to the statistics of the ECOBA (European Coal Combustion Products Association), of which Greece is a member, in 2016, more than 192 mt of fly ash was produced in Europe. Coal fly ash is utilized directly as a raw resource or additive

material by the construction industry, but large unutilized quantities of fly ash are treated by stockpiling, a practice that raises environmental concerns. Statistics on coal fly ash commercialization differ from country to country. The United States and certain countries in Europe have high utilization rates. The 15 ECOBA countries appear to be reusing 92% of the fly ash produced (Denmark and Italy recycle 100% of the total production), while there are insufficient data for the rest of Europe, and about 10% is repurposed in countries like China and South Africa [27].

Understanding the behavior of specific materials, such as fly ash, in leaching tests is a crucial step towards gaining a comprehensive understanding of the mode of occurrence, binding, and leaching characteristics of the contained metals. This knowledge, in addition to metal enrichment, can be instrumental in designing targeted, and therefore efficient, extraction procedures for metal recovery. The sequential extraction techniques have frequently been used as a leaching test to quantify the amounts of metal elements present in soils as well as to analyze their presence and association characteristics within soils [28–30] but also within fly ashes [28,31,32]. Among these techniques, sequential extractions proposed by Tessier and the European Community Bureau of Reference (BCR) are the most widely applied. In the present study, those two techniques were employed to identify the prevailing forms and associations of Li in the coal ashes under investigation.

2. Materials and Methods

Fly ashes from thermal power plants located in five different areas in Greece, which are depicted in Figure 1, were studied, namely Achlada (ACH), Ag. Demetrios (AGD), Amintion (AMI), and Kardias (designated as ACH, AGD, AMI, and KAR, respectively) in northern Greece, and Megalopolis (designated as MEG) in Peloponnesus, Greece. In addition, four samples from the Ag. Demetrios power plant collected at different dates (1998–2018) were also 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 to being used for characterization analyses and sequential extraction experiments. The samples underwent no crushing before being subjected to characterization and extraction experiments. Particle size distribution (using Laser Mastersizer S equipment) and the specific surface area (BET method) of the samples were determined. All the reagents used for the analyses and extraction experiments were of analytical quality and purchased from Sigma Aldrich, Steinheim (Germany). The sequential extraction experiments were performed in duplicate and the reported results are the corresponding mean values.

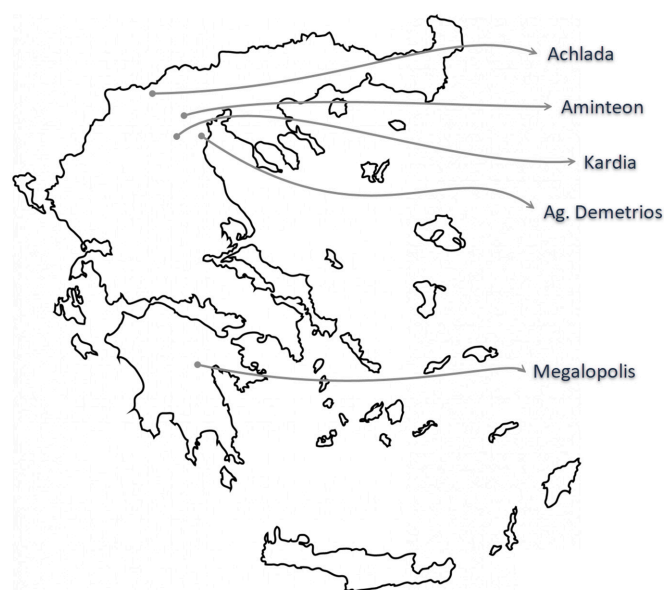


Figure 1. Sampling areas.

2.1. Samples' Characterization

2.1.1. Mineralogical Analysis

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. Diffra_cplus EVA by Bruker AXS and Seifert Autoquan software (version no. 2.8) were employed for qualitative and semi-quantitative analysis, respectively.

2.1.2. Chemical Analysis

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.

2.1.3. Li Content Determination

The Li content of the samples was determined by inductively coupled plasma mass spectrometry (ICP–MS) after total dissolution by acid digestion. For total dissolution an aliquot of 0.25 g sample was treated twice with an acid mixture containing concentrated nitric and hydrofluoric acid and subsequently with an acid mixture containing concentrated nitric and hydrochloric acid in PTFE containers. Each digested solution was steamed to almost dry heated in a water bath at 80 °C. After total dissolution, the resulting solution was acidified with 5% nitric acid, diluted to 50 mL and stored in plastic containers in the refrigerator until used for Li quantification by ICP–MS. For the analyses, the 7900 ICP–MS system by Agilent was employed. The results are reported in Li mg/kg produced using the appropriate calculations, taking into account the sample dissolution process (0.25 g sample to 50 mL solution).

2.2. Sequential Extractions

For the sequential extraction experiments, three samples were chosen. ACH and MEG samples were chosen because they have the highest Li content, and AGD was chosen because it differs in its mineralogical composition (less amorphous material and higher calcite and micas).

An aliquot of 1 g sample was transferred to a 50 mL centrifuge tube, and the sequential extraction experiments were carried out following the procedures described in detail by Park et al. [28]. With the Tessier sequential extraction technique, five fractions were obtained, namely the exchangeable fraction, carbonate-bound fraction, Fe-Mn oxide-bound fraction, organic matter-bound fraction, and residual fraction from the five steps of the procedure, respectively. With the BCR sequential extraction technique, four fractions were obtained, namely the exchangeable and weak acid soluble fraction, reducible fraction, oxidizable fraction, and residual fraction from the corresponding four steps of the procedure. In the present study, the above-described sequential extraction techniques were applied with a slight modification as far as the last step (Step 5 and Step 4 for leaching tests, Tessier and BCR, respectively) is concerned, that is, in order to identify the Li residual fraction, we proceeded to total dissolution by acid digestion (mix the concentrate of HNO₃, HF, and HCl) in PTFE beakers of the ash recovered in the penultimate step of each process as described in detail in Section 2.1.3. The concentration of Li in the supernatant solution, produced during each sequential extraction step, was subsequently measured by ICP-MS and the fraction of Li% that is leached in each step was calculated.

3. Results and Discussion

3.1. Sample Characterization

The particle size distribution of the samples varied between 1 and 140 μm . The KAR sample exhibited a size range of 1–90 μm , while the AGD sample ranged from 2 to 110 μm . The other samples (ACH, AMI, MEG) had a size range of 3–140 μm . The specific surface area of KAR was 5.1 m^2/g , for AGD, 2.6–2.9 m^2/g , and for ACH, AMI, and MEG, 3.2–4.2 m^2/g .

3.1.1. Mineralogy

The results of the mineralogy of the samples are illustrated in Table 1 and Figure 2. Mineralogical analysis reveals that amorphous material, represented by a broad peak (amorphous hump) at angles lower than $\sim 10^\circ$, is the most abundant constituent of all samples, with the ACH sample demonstrating the highest amorphous content (63%), and AMI and MEG following with 54 and 53%, respectively. The AGD and KAR samples appear to have the lowest (33%) amorphous content. This is a result in accordance with the literature [23–25,33–37], where fly ashes are reported to contain significant amounts of amorphous glassy material. The main mineral phases that are encountered in the samples are calcite (12 and 22% for the samples AGD and KAR, respectively), feldspars (11 and 14% for the samples ACH and MEG, respectively), quartz (12% for the samples AGD and MEG), and anhydrite (10 and 9% for the samples AGD and KAR, respectively). In addition, only the ACH sample appeared to contain mullite (10%), a mineral typical for high-alumina fly ashes that could be associated with elevated Li contents [6,17,18]. Finally, it is worth noting that since micas and pyroxenes could include Li-containing phases (muscovite and diopside), small quantities of micas (4 and 3% for samples AGD and KAR, respectively) and pyroxenes (5 and 3% for samples MEG and AMI, respectively) were identified in the samples studied.

Table 1. Mineral and amorphous content in coal ashes (% semi-quantitative).

% Mineral Phase	AGD	ACH	AMI	KAR	MEG
Anhydrite (CaSO_4)	10	1	7	9	5
Hematite (Fe_2O_3)	1	1	-	1	3
Calcite (CaCO_3)	12	-	6	22	1
Portlandite [$\text{Ca}(\text{OH})_2$]	1	-	-	-	-
Lime (CaO)	9	-	-	1	-
Gehlenite [$\text{Ca}_2\text{Al}(\text{AlSiO}_7)$]	4	-	8	8	4
C2S (Ca_2SiO_4)	3	-	4	6	2
Brownmillerite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$)	4	-	3	5	-
Feldspar [$(\text{Ca,Na})\text{Al}_{1-2}\text{Si}_{2-3}\text{O}_8\text{-KAlSi}_3\text{O}_8$]	6	11	10	6	14
Quartz (SiO_2)	12	8	4	5	12
Mica [$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F,OH})_2$]	4	1	1	3	-
Pyroxene [$(\text{Ca,Mg,Fe,Al})\text{Si}_2\text{O}_6$]	1	2	3	1	5
Spinel (MgAl_2O_4)	-	3	-	-	1
Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)	-	10	-	-	-
Amorphous	33	63	54	33	52

No significant difference in mineralogical analysis was observed for the AGD samples for the period studied. The results show that only SiO_2 and lime contents appear to be more than double in the most recent sample, with the rest of the phases remaining almost the same throughout the years. Even though those constituents are not Li-bearing phases, such fluctuations could influence a recovery process and should be taken into account.

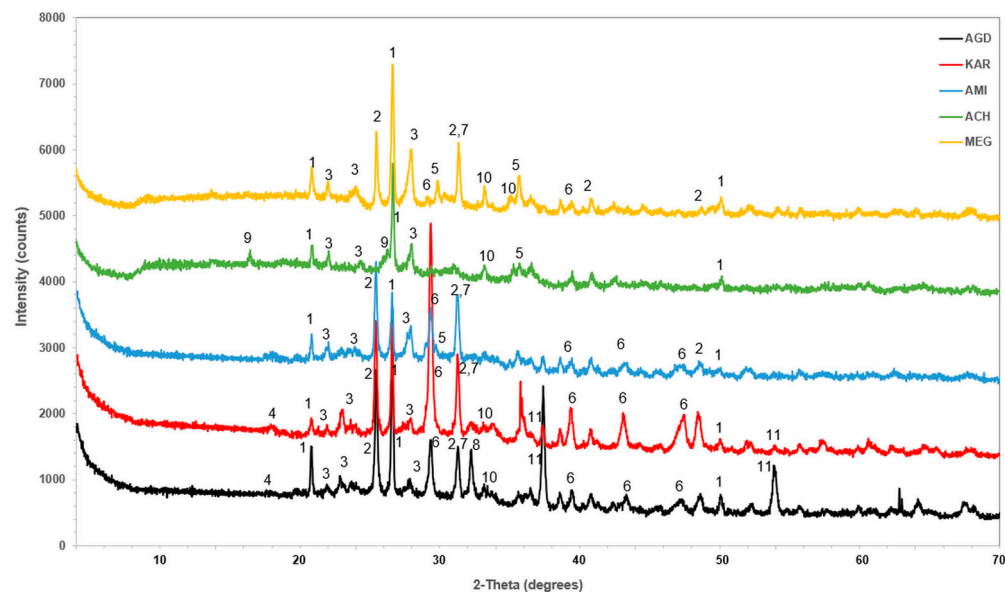


Figure 2. Samples' mineralogy. 1: Quartz, 2: anhydrite, 3: feldspar, 4: mica, 5: pyroxene, 6: calcite, 7: gehlenite, 8: C₂S, 9: mullite, 10: hematite; 11: lime.

3.1.2. Major Elements

The results of the major elements' analysis, expressed as the weight percent (wt%) of metal oxides, are illustrated in Table 2. The major element analysis is, as expected, in accordance with the mineralogical analysis. The elements silicon and aluminum appear to be the major components of all samples with the exception of calcium, which is the major component in the case of the KAR sample. No significant differences in chemical analysis were observed for the AGD samples for the period studied.

Table 2. The major elements (as oxides%) and corresponding loss on ignition (LOI) for the studied fly ash samples.

Major Elements	AGD	ACH	AMI	KAR	MEG
Na ₂ O	0.2	0.2	0.2	0.5	0.6
CaO	30.8	5.3	25.2	40.4	17.8
Al ₂ O ₃	13.8	25.3	15.6	11.8	17.6
Fe ₂ O ₃	5.3	9.5	7.3	5.2	11.0
SiO ₂	36.6	49.2	40.9	27.5	43.1
MgO	4.1	3.7	3.4	4.0	3.1
K ₂ O	1.1	2.6	1.1	0.7	1.7
TiO ₂	0.8	0.9	0.8	0.5	0.8
P ₂ O ₅	0.1	0.1	0.1	0.2	0.1
SO ₃	7.1	2.6	4.6	7.1	3.6
LOI	0.1	0.5	1.6	2.0	0.6
SUM	100	100	100	100	100

The highest concentration of Al₂O₃, 25.3%, is reported for the ACH sample, with the MEG sample following with 17.8% Al₂O₃ and the KAR sample exhibiting the lowest content. Loss on ignition, which is also reported in Table 2, is low (<2% for all samples), suggesting that unburned carbon in the samples studied is also low at <2%.

3.1.3. Li Content

The Li content of the samples is illustrated in Figure 3. The highest Li content, 256 mg/kg, is reported for the ACH fly ash sample; MEG fly ash follows with 211 mg/kg, and the lowest concentration, 95 mg/kg, is observed for the AGD 2002 sample. The Li

contents for the AGD samples fluctuated between 95 and 126 mg/kg, with the most recent one exhibiting the highest concentration. The reported results are in accordance with the literature [6,14,38]. The Earth's crust is reported to contain an average of 33 mg/kg Li, while coal ashes worldwide are reported to contain 66 mg/kg Li [39]; therefore, all the fly ash samples studied could be considered enriched (enrichment factor >1 compared to ashes worldwide and >2 compared to the Earth's crust). The relatively high Li content, 256 mg/kg, which corresponds to 0.06 weight percent (wt %) of lithium oxide (Li_2O), encountered in ACH fly ash is comparable to industrial-grade Li-bearing pegmatite deposits in China [19,21].

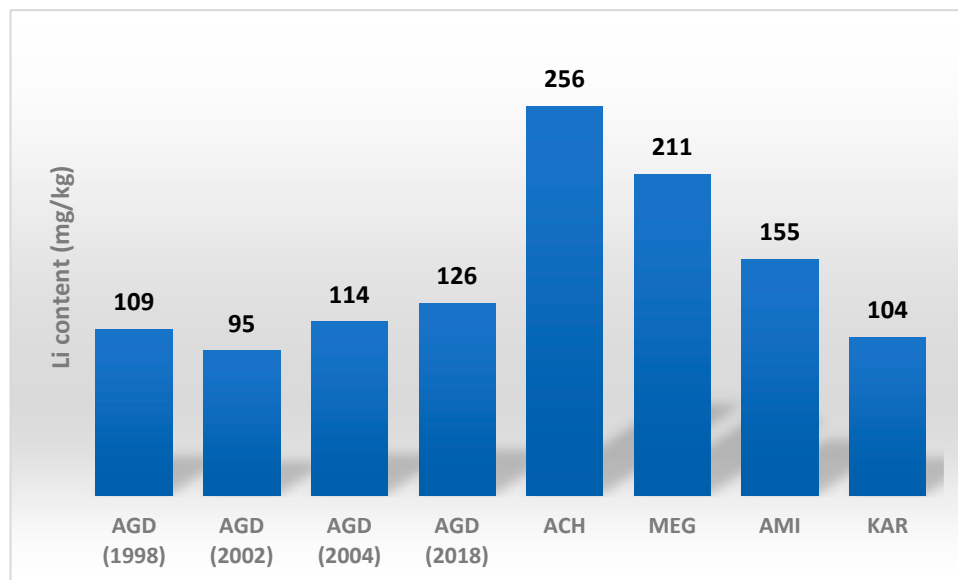


Figure 3. Li contents (mg/kg) for the fly ash samples studied.

To study the correlation between the major elements and minerals identified, with the Li contents measured, the linear correlation coefficients were used. As depicted in Figure 4, Li showed a very strong positive correlation ($r^2 = 0.9$) with Al content and amorphous material. For the rest of the elements and minerals, poor to intermediate correlation was observed, while calcium exhibited negative correlation.

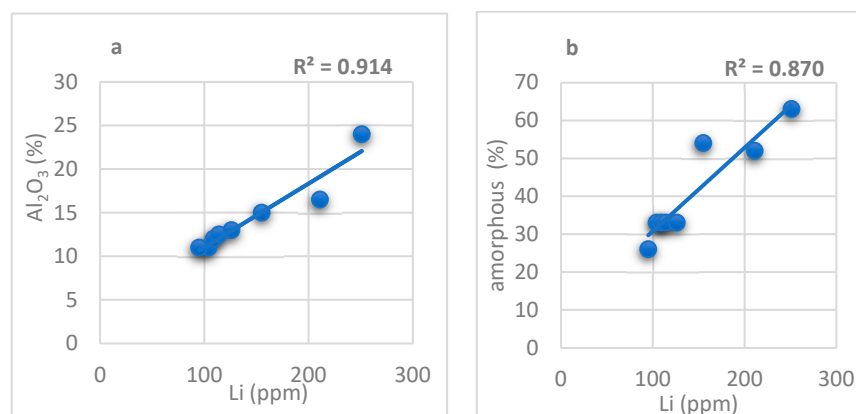


Figure 4. Li correlation with (a) Al content and (b) amorphous material.

Li's strong positive correlation with Al observed is in accordance with the literature [18,20,21], where several researchers report that high-alumina coal fly ashes could be regarded as a potential Li secondary resource [26,40,41]. The strong positive correlation between amorphous material and lithium content, if combined with the fact that no Li-bearing

phases were identified in the ACH fly ash sample, which appears to have the highest Li content, could suggest that Li is hosted in the amorphous glassy material of the samples, a suggestion that has also been reported in previous research [20,21].

3.2. Sequential Extraction Experiments

The results of the sequential extraction experiments are illustrated in Figure 5, where the fraction of Li % that is leached in each step is depicted. As shown in Figure 5, only slight differences can be observed between the two sequential extraction techniques applied. Relatively small quantities of Li are leached during the early stages of the extraction experiments, with the highest amounts, up to 95% for the ACH sample, being extracted in the final step.

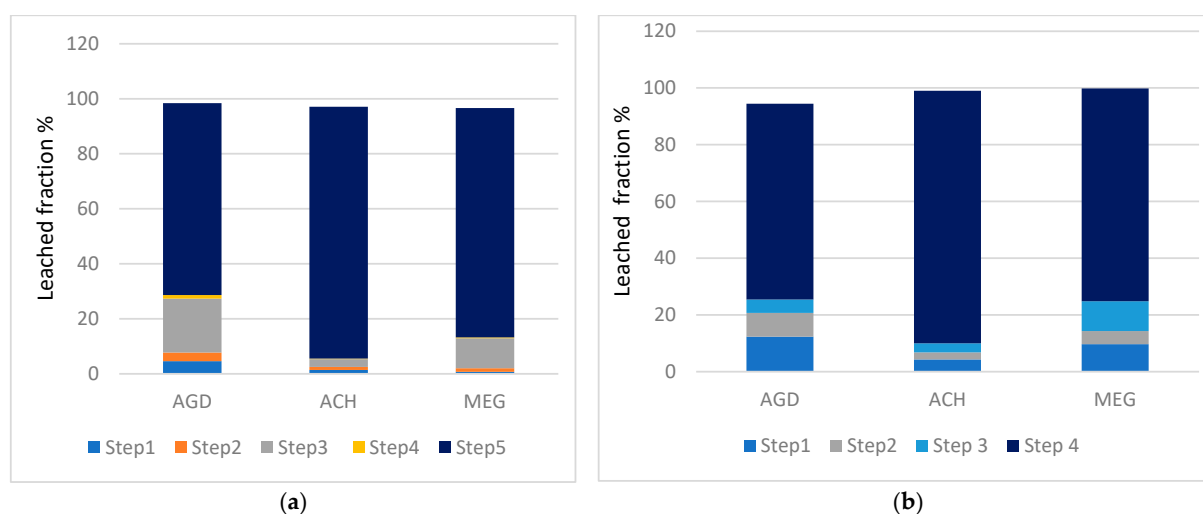


Figure 5. Results of (a) Tessier and (b) BCR sequential extractions of fly ashes.

The results of the Tessier sequential extraction method for the AGD and MEG samples show that the first three steps of the procedure extract 27.3 and 14.0% of the total Li content, respectively, with the highest fraction being obtained in the third step. On the contrary, the ACH sample only releases 5.1% of its total Li content during the first three steps of the method. In all the samples, the fourth step of the method leaches less than 1% of the total Li content, which is consistent with the low amount of organic matter present in the fly ashes. A similar pattern is observed when the BCR sequential extraction method is applied, with 69%, 75%, and 89% of the total Li content for the AGD, MEG, and ACH samples, respectively, remaining in the residual fraction. Therefore, it can be inferred that most of the Li present in the samples studied exists in forms that are strongly attached to the mineral matrix and not easily released by the corresponding extraction media.

4. Conclusions

The Li contents of the fly ash samples studied fluctuated between 95 and 256 mg/kg. Among the samples studied from the Ag. Demetrios power plant, which were collected at different dates, no significant differences were observed as far as the Li and major elements contents are concerned, while as far as the mineralogy is concerned, the results show that only SiO₂ and lime contents appear to be more than double in the most recent sample, with the rest of the phases remaining almost the same throughout the years. The fly ash from Achlada (ACH) appears to possess the highest lithium content, 256 mg/kg Li. This value corresponds to 0.06 weight percent (wt %) of lithium oxide (Li₂O) and is comparable to the lithium content found in some industrial-grade Li-bearing pegmatite deposits. It is observed that there is a strong positive correlation between the lithium content and the amorphous material in the samples, and since no lithium-bearing phases are detected in the ACH sample (the fly ash with the highest Li content and the highest amorphous

content), it can be concluded that the lithium is mainly hosted in the amorphous glassy material of the samples studied. The sequential extraction experiments revealed that most of the Li (up to 95% in the case of ACH) present in the samples studied is strongly bound to the mineral matrix and not in readily released forms. Further research with sample morphology characterization techniques, such as scanning electron microscopy, and tests that would selectively remove amorphous material, such as extraction with diluted HF or NaOH solutions, would be useful to gain a better insight into Li associations with the major constituents of the samples, contributing to the design of more targeted and therefore more efficient Li recovery procedures.

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