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Mineralogical examination of biomass ashes: a preliminary study for potassium enrichment and phosphoric acid (H_3PO_4) production

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Research Article

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Biomass Ash,
Langbeinite, Phosphoric Acid, Potassium Sulphate.

ABSTRACT

In this study, biomass fly ash was investigated and determined by XRD (XRay Diffractometer) to be predominantly langbeinite, aphthitalite, sylvine, apatite and hydroxyapatite. An alkaline leaching study was carried out on the material in a glass reactor at l/s ratio 4 temperature 60°C at pH 12.85 and after drying was analyzed by ICP (Inducted couple plasma). The crystal structure composition of K_2SO_4 72.28% and potassium content of 33.47% (w/w) was recovered. The elemental transformations in this leaching process were: K 74.16%, Mg 0.55% was found to be 0.8%. It was found that a minimum of 4.84 g H_2SO_4 per 100 g fly ash was required to precipitate the $Ca(OH)_2$ migrated into the liquid solution and the overall leaching efficiency was found to be 29.85%. In the alkaline leaching process, potassium was found to be easily recovered from each biomass ash. By adding 40 g H_2SO_4/100 g biomass waste remaining after leaching, a phosphorus recovery of 74.9% was observed. In this preliminary study, unsatisfactory results were obtained in obtaining the industry standard H_3PO_4. The reason for this is that the Al, Mg and K in the fly ash are subject to selective dissolution as a result of working at high pH in the alkaline leaching process.

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1. Introduction

Biomass ashes contain large differences in classification and structure compared to coal-based thermal power plant ashes. Currently, the ASTM C618-19 (2019) standard is used for this purpose. In order to classify the origin and structure of biomass ashes, the use of a triangular diagram based on the K_2O, CaO and SiO_2 w/w contents as a 3-phase diagram has been recommended (Zhai et al., 2021).

Biomass ashes can be accepted as secondary phosphorus and potassium sources due to their high phosphorus and potassium contents. In recent years, the number of thermal power plants with different designs suitable for biomass combustion has increased rapidly. A new alternative material has emerged to meet the limited phosphate and potassium requirements due to the structure of these ashes. In the characterization study of biomass ashes by Çöteli and Karahan (2023), chemical analyses were carried out and it was found that the potassium in the ash was completely soluble in water and had a highly alkaline character.

Potassium is found in many igneous rocks such as feldspar (potassium aluminum silicate), $KAlSi_3O_8$ (leucite) and mica, KH_2Al_3 (SiO_4) three. As these

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rocks break down and dissolve, potassium mixes with the soil and water. Potassium chloride deposits are found in almost all salt deposits associated with sodium chloride. Some important potassium minerals are leucite, $KAlSi_2O_6$; glauconite (a complex silicoaluminate structure of varying composition); sylvine (KCl), carnallite ($KCl-MgCl_2.6H_2O$), langbeinite (K_2SO_4. $2MgSO_4$) and polyhalite ($K_2Ca_2Mg(SO_4)_4.2(H_2O)$) (Patnaik, 2002).

Although Krishnamurty et al. (2008) stated that potassium carbonate (K_2CO_3) is predominantly found in wood ash, the study of the calcination temperature in thermal power plants and the almost complete absence of carbon content in the ash suggest that it is present in different forms. In order to recover potassium, its mineralogical structure must be clearly identified. Currently, the biomass ash waste potential in our country is around 600 tonnes/day, which corresponds to 72 tonnes of K_2O/day. An alternative way to solve our country's potassium problem has been opened, mainly through good national management planning of existing material resources. Although some small private companies are still working on it, industrial adaptation and economic production cannot be achieved.

Although there is no sodium salt problem in our country in terms of reserves and production, there is no discovery and production of potassium ore and salt due to the geological structure of our country. A long time ago, especially in the 1980s, studies were carried out on the production of potassium chloride from İzmir Çamaltı Brine Salt Works, and although there were studies aimed at obtaining potassium from some clay minerals (such as potassium feldspar), studies were carried out to meet satisfactory consumption. ALKİM (2023) stated in its annual report that it uses imported potassium chloride and domestically produced crystalline sodium sulphate in the production of potassium sulphate. Russia and Belarus supply approximately 40% of the global potassium chloride market and are the countries closest to us logistically. The potassium sulphate capacity of the Alkim (Alkim Alkali Chemistry Company) - Dazkırı, Koralkim plants is 50,000 tonnes/year and K_2SO_4 production is done with H_2SO_4 via imported KCl. Until now, it has not been possible to produce enough different potassium salts to meet the import requirements in terms of potassium mining. The country's industry meets all its potassium needs through imports.

Furthermore, if we look at the import data of TÜİK (Turkish statistical institution, 2022), it can be seen that the foreign exchange from the fertilizer sector has reached $2.7 billion. Two of the main inputs to the fertilizer industry are the output of potash and phosphate mining.

In Burke (2021), ash management is important due to the increased use of biomass for energy production; burning unprocessed biomass in modern furnaces can produce small amounts of ash containing negligible persistent organic pollutants, and land application is possible due to low concentrations of contaminant metals. He noted that agricultural residue ashes contain high levels of potassium and useful phosphate, so could potentially be used as fertilizer. This highlighted the importance of recovering potassium from ash.

Although biomass has many uses in conventional agriculture, such as direct green manuring, composting and use for organic matter needs, small-scale thermal power plants for electricity generation have begun to grow rapidly as a result of the rapid increase in per capita energy consumption. The resulting fly ash has created an environmental and bio-waste and ash management challenge. Fly ash contents are never similar to coal based thermal power plant ashes and as an alternative secondary source of phosphorus and potassium for industrial waste recovery, studies on its use, recovery and product development have accelerated within the scientific framework.

In this study, the recovery of potassium compounds from biomass ashes from thermal power plants by dissolving them in water, their technological economisation, the outline of the process, their partial purification from impurities (such as Ca, Na) and their valorization in terms of mining as a 2nd stage industrial product (a mixture of K_2SO_4, KCl, NaCl and Na_2SO_4) are planned. The remaining solid valorized waste was studied to obtain H_2SO_4 and H_3PO_4. The aim was to develop a suitable process for economic production by determining potassium recovery and yield. The main objective is to obtain high value added products from the biomass ashes consisting of these agricultural waste fertilizers with special status. A feasibility study for industrial economic production was carried out.

2. Literature Review

Weast and Astle (1980) stated that potassium is difficult to dissolve due to its crystal structures being bound to other minerals and that it occurs in nature mainly as sylvine, carnalite, langbeinite and polyhalite minerals and is found in small areas in Germany, New Mexico, California, Utah etc. Particularly large potash resources are found in Saskatchewan at a depth of 3000 ft. It is also found in sea water and in salt deposits.

Civelekoğlu et al. (1987) stated that the main minerals of potash salt production are K and Al silicates which are insoluble in water and that potash salts are refined from water soluble and potassium containing solutions by methods such as dissolving and cooling in hot (KCl, from sylvine) or decomposition (KCl, from carnallite) with NaCl and $MgCl_2$ salts and that the basis of this process is understandable 2-3 phase diagrams.

Krupa et al. (2008) also carried out a study on the production of phosphoric acid on bone meal ash, which has the mineral structure of hydroxyapatite.

$$2Ca_5(PO_4)_3OH + 10H_2SO_4 + 18H_2O \rightarrow 6\ H_3PO_4 + 10\ CaSO_4\ 2H_2O$$

Bone meal was subjected to calcination at 600°C. 43% H_3PO_4 solution was formed after reacting with the ash and adding unreacted jibs. They were reacted at 90-95°C and H_2SO_4 was added, resulting in a product that contained 45% H_3PO_4. The solid part was separated, and by adding steam to remove some water vapor, commercial phosphoric acid containing approximately 75% and 54% P_2O_5 was obtained (Figure 1).

Zhai (2022) stated that the common mineral phases are calcite ($CaCO_3$), fair calcocite [$K_2Ca(CO_3)_2$] and arcanite (K_2SO_4) based on the XRD raw spectra of different biomass ashes. All of the wood ash burnt in the laboratory is dominated by the calcite phase, with small amounts of Arcanite and hydroxyl apatite [$Ca_5(P0_4)_3(OH)$]. This ash contains some calcite, arcanite, larnite (Ca_2SiO_4) and polyhalite

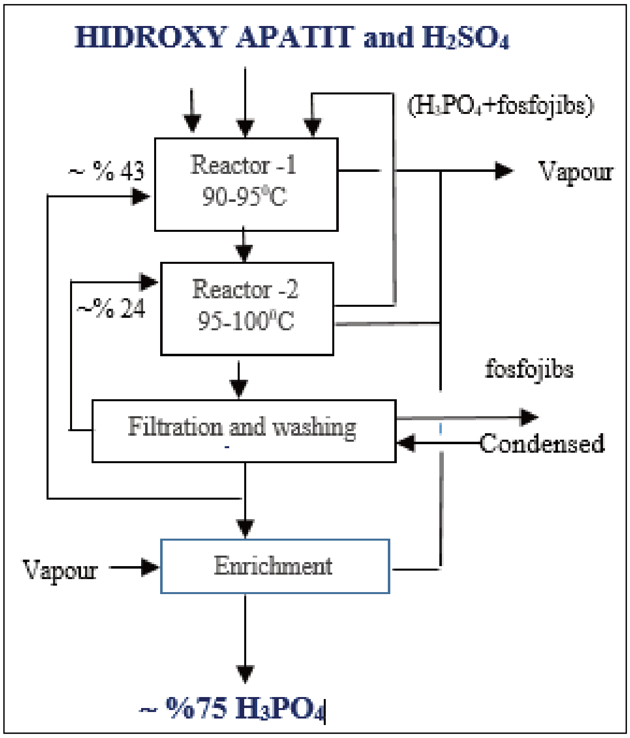

Figure 1- A brief representative description of the industrial production of phosphoric acid, from calcinated bones (Krupa et al., 2008).

[$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$]. In the example of industrial wood ash, quartz (SiO_2) and calcite are present. Lime (CaO) also contains some kalsilite (KAl_2SiO_4), gypsum ($CaSO_4 \cdot 2H_2O$) and some periclase (MgO) and sodium, calcium silicate ($Na_2Ca_3Si_2O_8$). Archonite and sylvine (KCl) have also been identified. Although the rice husk ash sample also consists mainly of SiO_2, the main mineral phase of cristobalite contains less quartz, while in another sample it consists mostly of quartz, and in both samples, there is some amorphous content of sylvine, arcanite and less kalsilite ($KHCO_3$). Minerals detected in XRD analyses in biomass ash samples, depending on the ash source; arcanite (K_2SO_4), calcite ($CaCO_3$), cristobalite (SiO_2), fairchildite [$K_2Ca(CO_3)_2$], hydroxyapatite [$Ca_5(PO_4)_3(OH)$], calcilite (KAl_2SiO_4), kaolinite [$Al_2Si_2O_5(OH)_4$], larnite (Ca_2SiO_4), lime (CaO), periclase (MgO), polyhalite [$K_2Ca_2Mg(SO_4)_4 . 2H_2O$], silica ($SiO_2$), sodium calcium silicate ($Na_2Ca_3Si_2O_8$) and sylvine (KCl).

Regarding phosphorus recovery, Becker (1989) explained the fundamentals of phosphorus recovery economics, the differences between processes, how wet and dry phosphoric acid production differs, and how thermal processes vary based on the material structure. Although there are project studies called RecoPhos using a carbon-lime mixture at 1300-1900°C thermally, it is not thought to be as economical as the wet process. It is difficult to work due to the difficulty in reaching the temperature. Trial production is still ongoing, and large-scale production seems only possible by obtaining H_3PO_4 through the wet process. It seems to be an alternative way to obtain high purity phosphoric acid with low heavy metal contamination. This can be especially useful in food applications. Additionally, biomass ashes are a cleaner material than natural waste sludge and rock phosphate deposits. In this case, the mineralogical structure of the material is key. The process called Recophos is not actually a new process, but is a modified version of the electric furnace process (Austin, 1985), which was developed as an alternative for use on rock phosphates in the 1920’s in case of cheap electricity supply.

$$2Ca(PO_4)_2+6SiO_2+10C \rightarrow 6CaSiO_3+P_4+10CO$$
$$\Delta H=-3055 \text{ kJ}$$

Donatello and Cheeseman (2010) gave an empirical formula for P extraction from waste sludge ashes, as in Franz (2008).

Amount of g H_2SO_4 per 100 g material:

$$(1.479*CaO+0.962*Al_2O_3+0.614*Fe_2O_3+$$
$$2.433*MgO+1.582*Na_2O+1.041*K_2O)-$$
$$(0.691*P_2O_5+1.225*SO_3\%)$$

The empirical approach is actually similar to Nunn and Dee (1954). Provided that the liquid/solid ratio was 20, it was dissolved with H_2SO_4 solution at a concentration of 0.19 mol/l for 120 minutes, and then the liquid part of the filtered mixture was passed through cation exchange resin and analyzed for Zn, Fe, Mg, Ca, Al, P and SO_4^{2+}. The final product had a concentration of approximately 1% H_3PO_4 and could reach 85% H_3PO_4 concentration by vacuum distillation.

Raupenstrauch (2015) explained the RecoPhos process for obtaining H_3PO_4 from industrial city biomass waste ashes. With 80% waste sludge ash (SSA) (8% P content) material at a feeding rate of 10kg/h, 10% C and 10% lime mixture, the P recovery in the melting furnace operating at 1900^0C increased to 90%, and the heavy metals in the ash were eliminated. He explained that H_3PO_4 could be produced by extracting the gas phase in water.

Lijian et al. (2019) stated that biological wastes such as meat and bone meal and poultry manures are used as energy sources in industrial facilities, but the phosphorus in the biomass ashes remaining after combustion is thrown away without being used, and to encourage their use, biomass ashes from industries are highly alkaline with pH values as high as 13. The content is high in phosphorus and calcium. X-ray powder diffraction (XRD) reveals hydroxyapatite and potassium sodium calcium phosphate. Nearly 90% of phosphorus can be removed by acid extraction (H_2SO_4); optimized acid consumption is 3 (they determined that it was 2–5.3 mol H+/mol P). Nearly 90% of phosphorus can be removed by acid extraction (H_2SO_4); optimized acid consumption is 3 (they determined that it was 2–5.3 mol H+/mol P). Nearly 90% of phosphorus can be removed by acid extraction

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Gowariker et al. (2009) explained that the ash produced by burning wood is rich in potassium (in the form of K_2CO_3) and is useful for correcting the pH of acidic soils, is also explained the Mannheim process, which is the production of K_2SO_4 from KCl. This process is a 50% K_2O process in which KCl reacts with H_2SO_4, yielding excess $KHSO_4$, KCl and HCl as a gas.

Schultz et al. (2000) described the production of potassium fertilizer from the natural complex salts kainite ($KCl.MgSO_4.3H_2O$) and langbeinite ($K_2SO_4.2MgSO_4$) and Carpathian poly-minerals. In the process, kainite is leached to form schonite ($K_2SO_4.MgSO_4.6H_2O$) and $MgCl_2$ is separated. He stated that schnite is separated into K_2SO_4 and $MgSO_4$ by leaching in the same way.

Wang et al. (2016), potassium recovery by leaching method on an ash sample containing 39.44 mg/g volatile matter, 158.92 mg/g fixed carbon, 51.64 mg/g K and 28.56 mg/g Mg. In the leaching process with H_2SO_4, the pH was adjusted to 6.1, the liquid/solid ratio was 3 and the temperature was 75°C. At the end of 30 minutes, the pH increased to nine and a K recovery efficiency of 86.4% was achieved. In his study, he observed that the solubility of potassium is independent of pH and that low pH leads to the formation of $CaSO_4$, which causes pH collapse. In addition, the world's potash resources are limited and potassium dolomite deposits (8.21%) could be an alternative. This process involves calcining the material ground below 74 microns with Na_2CO_3 at 840°C, leaching with water and CO_2 for 2 hours at a l/k ratio of 8-10, evaporation and crystallization, and K_2CO_3.

Akgül and Yoncacı (2021) gave different classifications on the classification of the thermal power plant producing fly ash and its classification is siliceous (S), silicocalcic (CS), ferrosilicic (FS) and ferrocalcic (FCS). In this classification, he also stated that they are categorized into three dominant tendencies such as high acid (HA), medium acid (MA) and low acid (LA) according to the sum of Si, Al, K, Ti and P oxides.

Li et al. (2015) found that aluminum and iron phosphates, which are difficult to use at high temperatures, react with lime (CaO) in the environment at different temperatures to the apatite form $Ca_3(PO_4)_2$, from which phosphorus recovery is easier. He explained that aluminum and iron are oxidized as Al_2O_3 and Fe_2O_3 and phosphorus is bound to Ca in the form of apatite.

Çağan (2014) stated that the general formula of apatite is $X_{10}(TO_4)_6Z_2$, and instead of X, Ca, Sr, Pb, Cd and Ba; P and As instead of T; OH, F, Cl can be entered instead of Z.

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

According to its reaction, it is possible to produce it in pure form. Hydroxyapatite has high biocompatibility; he stated that not only can the body easily accept it, but it can also create a suitable environment for the growth of bacteria, which are other biological structures, and can be used especially in dental implants.

Karabacak (2021) revealed some commercial processes for phosphorus recovery from waste sludge ash by listing the principles and effects/products. The material he works on is BUSKİ samples and the ash content is P_2O_5 17.36-11.49% in two different samples; K_2O content is between 3.70-3.16 and used H_2SO_4 solution at different concentrations to transfer the phosphorus in the ash to the solution.

In KTÜ (2017) and Tor (1991) by adding liquid ammonia (NH_4OH or $(NH_4)_2S$) to a solution containing Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, It has been found that $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, MnS, NiS, CoS, FeS, ZnS precipitate while Ba^{2+}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ remain in solution.

Millsaps et al. (2021) determined the required H_3PO_4 ratio in a collaborative study involving acidification with H_3PO_4 for the production of phosphorus fertilizer from poultry manure, the total and water-soluble P_2O_5 content of the final product, and the granulation process. In the ideal study, 0.6 kmol H_3PO_4 per 100 kg ash was found. However, the reaction time is very short and it is stated that the granulation process of the paste material should be started immediately within a maximum of 4 minutes.

As stated by Bogusha et al. (2018), this is an increasing problem due to the rising number of biomass power plants in numerous countries. It is therefore essential to be comprehensively characterized biomass ashes, with particular focus on the elemental composition and solubility of nutrients (e.g., K and P) and contaminants. Furthermore, these residues can be utilised for soil nutrition. All biomass ashes studied were alkaline and exhibited high concentrations of P, K and Ca, which are essential for their potential utilisation. He stated that it contained the following: Phosphorus is present in: 1) Bottom ash contains apatite and other phosphates, including potassium hydrogen phosphate and potassium iron phosphate, which are produced when poultry litter is incinerated. 2) It is reported that this material originates from poultry litter incineration and contains potassium, sodium, calcium phosphate. Potassium is mainly present as sylvine, arcanite and some phosphates. Phosphorus, calcium and magnesium are difficult to leach with water, and recovery of potassium and phosphorus from these materials must be done carefully. It has been documented that this is a viable method.

Sof et al. (2021) and Çöteli and Karahan (2023) also studied the method of acidifying the material with H_2SO_4 in the production of PK and NPK organic and inorganic fertilizers in the fertilizer sector. The basis of the developed production method is the complete acidification of the phosphorus in the ash to make it soluble in water. The main purpose of the study is to use the existing material in the inorganic and organic fertilizer sector.

Çöteli and Karahan (2023) investigated the chemical composition of the ashes of the biomass thermal power plants installed in Turkey as a function of time and found that the ashes of the biomass thermal power plants had a chemical composition as shown in Table 1.

Puspita and Susanto (2021) also worked on the development of a new technique for the recovery of potassium salt from biomass ash extraction solution containing a mixture of KCl, NaCl, $MgCl_2$ and $CaCl_2$. The process involves partial evaporation of the solution, followed by the addition of ethanol and further evaporation. In their study, they showed that KCl can be recovered in a different way than in traditional studies.

Table 1- A chemical characterization of Turkish biomass thermal power plant fly ashes (Çöteli and Karahan, 2023).

	Average%	**Max %**	**Min %**
Al_2O_3	4.75	16.97	2.88
CaO	16.05	19.24	10.57
Fe_2O_3	1.94	7.03	0.32
K_2O	12.75	27.0	2.94
MgO	6.56	11.50	1.19
Na_2O	6.47	27.38	4.79
P_2O_5	12.38	19.53	4.98
	mg/kg		
As	15	27	3
Cd	1	3	0
Co	8	25	3
Cr	121	995	16
Cu	432	1024	141
Pb	232	691	14
Zn	950	3997	100
Note: 1-Ash samples have a highly alkaline character and the pH (1/10) is in the range of 11-13 depending on the sample. 2-1 Valent cations and anions are completely soluble. 3-P_2O_5, it is 0.5-1.5% water-soluble, depending on the cation bounds to.			

3. Technological Studies

3.1. Material Used

The sample (fly ash) (Figure 2) obtained from the 20 MW installed capacity fluidised bed thermal

Figure 2- Biomass fly ash studied.

power plant located in Sakarya-Akyazı district has a particle size completely below 50 microns and the sample, which is believed to have been calcined (containing CaO, MgO, etc. material) due to the high temperature at the outlet of the plant, was placed in a closed package. The plant burns more than 50% of agricultural waste, in particular poultry waste and poultry manure.

3.2. Chemical, XRD and SEM (Scanning Electrone Microscope) Analyses

The results of the ICP analysis are given in Table 2 after dissolution in aqua regia. It is a material with the status of the second source of potash and phosphate.

The XRD analyses were carried out on the Bruker-D-8 Advance, the values obtained from the XRD diffractogram were evaluated in the "HighScore Plus" software and the mineral structures contained therein were determined.

The powder sample to be examined on the FEI Inspect F50, FEG-SEM instrument was subjected to SEM-EDS (Elemental Analys in scanning electron microscope) analysis after gold-palladium coating. The results of these analyses were SEM photographs and EDS graphs showing the elements contained.

The analyses of fly ash using SEM+EDS at the 1st point range, at the other 2 points and as an average are given in Table 3 as percentages. The ICP analyses were compared.

Table 2- Chemical composition of the studied fly ash material.

ELEMENT	VALUE	ELEMENT	VALUE	ELEMENT	VALUE
Al %	2.00	As ppm	15.49	Mn ppm	3069
Ca %	15.81	Ba ppm	258.61	Ni ppm	60
Fe%	1.09	Cd ppm	1.60	Pb ppm	19
K%	13.47	Ce ppm	10.11	Sb ppm	4
Mg%	4.33	Co ppm	7.19	Sr ppm	382
Na%	2.06	Cr ppm	39.24	V ppm	45
P%	4.93	Cu ppm	475.35	W ppm	39
S%	6.50	La ppm	6.99	Zn ppm	2880
				Zr ppm	32

Table 3- Chemical analysis of fly ash at the marked point by SEM-EDS.

ELEMENT	Point 1	Point 2	Point 3	Average	ICP
	% w/w				
Al	1.10	1.07	1.13	1.10	2.00
Ca	14.12	14.97	13.89	14.32	15.81
Cl	6.48	0.60	6.53	4.53	-
Fe	0.90	0.73	1.30	0.97	1.09
K	21.33	14.51	21.63	19.16	13.47
Mg	3.14	3.43	3.26	3.27	4.33
Mn	0.10	8.22	0.11	2.81	0.3
Na	4.31	8.31	3.94	5.52	2.08
O	34.19	36.31	34.02	34.84	-
P	4.70	12.21	4.82	7.24	4.93
S	7.61	6.33	7.41	7.12	6.50
Si	2.02	1.52	1.95	1.83	-

3.3. XRD Analysis on the Material and Pointwise (at the Marked Point) Mineralogical Composition Determination with SEM-EDS

As a continuation of the study, the crystal structure of Ca, K, Mg, P, compounds was determined by XRD to determine the mineral structure of the material.

When biomass ash (Figure 3) is subjected to XRD analysis, the main structure contains potassium minerals; as, in ascending order, sylvine (KCl), aphthilatate ($Ca_3NaO_8S_2$), (K, Na)$_3$Na $(SO_4)_2$, langbeinite [K_2Mg_2 $(SO_4)_3$] and a very small amount of $K_4[Fe\,(CN)_6]$-$3H_2O$ in its aqueous form were observed. In addition, $Ca(OH)_2$, CaO and SiO_2 contents are also present and the ash structure has indeed reached a new mineralogical structure in the form of calcination. In terms of phosphorus, the dominant structure is apatite $Ca_{10}(PO_4)_6(OH)_2$ and hydroxyapatite.

After the determination of the main minerals in the biomass ash by XRD, an elemental mass balance was carried out for the elements Ca, Fe, Al, Mg, P, K, Na, S, with an acceptable margin of error (oxygen (O), hydrogen (H) and carbon (C) analysis was not carried out, it was considered as an equation with several unknowns (matrix solution) and the ratio of components and minerals in the material was determined as (w/w) using an Excel spreadsheet (Table 4).

Patnaik (2002) gave these compounds of Ca, Mg, Na and K collectively with their mineral names and CAS numbers (Table 5).

XRD analysis of the material indicated that potassium and magnesium compounds were predominantly in the form of langbeinite and sylvine whereas phosphorus was in the form of apatite and hydroxyapatite.

4. Experimental Studies of Phosphorus and Potassium Recovery and Enrichment

In terms of potassium recovery in the study, the principle that II-valued cations (except Al and Si) are insoluble in alkali, but K, Na compounds and I-valued anions are soluble in water (Weast and Astle, 1980; Green and Southard, 2019). The purpose of this is to obtain a cleaner solution as Ca, Fe, Cu, Zn, P and Mg do not enter the solution.

Firstly, the alkaline leaching under normal conditions; (120 min) l/s ratio of 5 and 10 was observed and visual difficulties were observed, pH control and then the elemental balance, which could be adapted to the industry by increasing the temperature, and the possible yield and final product composition were tested.

In the production of phosphoric acid, it was determined how much phosphorus content PO_4^{3+} could be recovered by reacting the purified waste product with K, adding the necessary H_2O+H_2SO_4 and filtering out impurities such as phosphoric gypsum.

4.1. Potassium Recovery Studies

Using the elemental solubility tables given in Green and Southard, (2019) it was investigated what

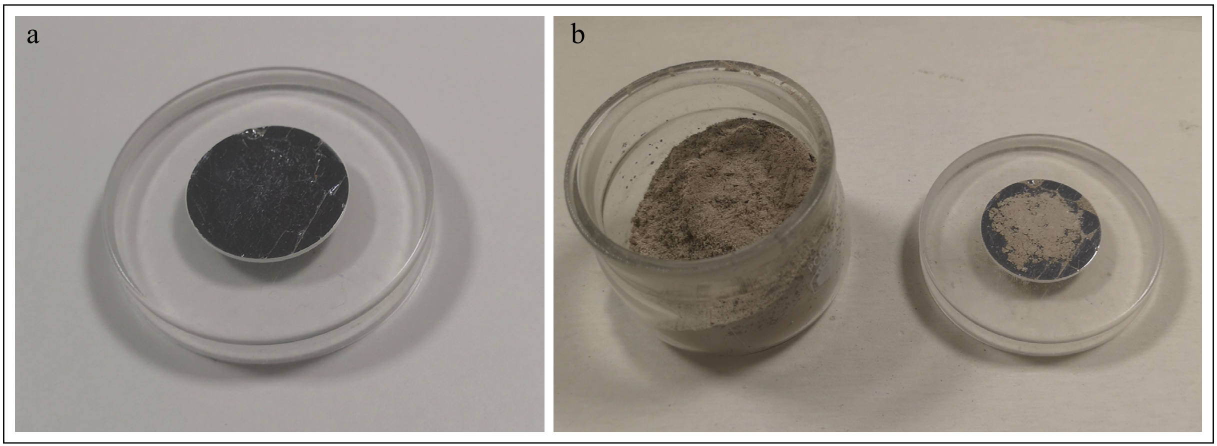

Figure 3- Sample preparation before XRD analysis of biomass ash, a) sample prepared for XRD, b) together.

Table 4- Determination of aproximately chemical composition in fly ash according to XRD and ICP analysis results[3].

COMPONENT	MW	QTY	%	Al	Ca	Fe	K	Mg	Na	P	S	Ref
Al_2O_3	101.96	4.00	4.00	2.00								Krupa et al., 2008
$Ca(OH)_2$	74	1.35	1.35		0.73							
$Ca(PO_4)_2$	230	1.62	1.62		0.28					0,44		
$Ca_{10}(PO_4)_6(OH)_2$	1004	22.20	22.20	0.00	8.84	0.00	0.00	0.00	0.00	4,11	0.00	
$Ca_5(PO_4)_3(OH)$	502	2.00	2.00		0.80					0.37		
CaO	56	7.20	7.20		5.14							
Fe_2O_3	160	1.56	1.56			1.09						Krupa et al., 2008
$K_2Mg_2(SO_4)_3$	**414**	**9.00**	**9.00**				1.70	1.04			2.09	
K_2SO_4	174	10.00	10.00				4.48				1.84	
$K_4[Fe(CN)_6]\cdot 3H_2O$	368.35	~	~									
KCl	74.5	12.44	12.44				6.51					
$MgCl_2$	95	8.00	8.00					2.02				
$MgSO_4$	120	1.50	1.50					0.30			0.30	
Na_2SO_4	142	1.00	1.00						0.32		0.32	
NaCl	59	4.45	4.45						1.73			
$NaKMg_2(SO_4)_3$	398	8.00	8.00				0.78	0.96			1.93	
SiO_2	60	5.68	5.68									Çöteli and Karahan, 2023
Σ		100.00	100.00	2.00	15.80	1.09	13.47	4.33	2.06	4.92	6.48	
ICP Analyses results % (w/w)				2.00	15.81	1.09	13.47	4.33	2.06	4.93	6.50	

Note: [1]Krupa et al. (2008) stated that Fe and Al phosphates decompose into Fe_2O_3 and Al_2O_3 at high temperatures.

[2]Silicon analysis was not performed in ICP, only the % SiO_2 amount from XRF analysis was taken for the 5.68% for 100 balances in Çöteli and Karahan (2023).

[3]Possible compounds of 3Al and Fe in the silicate structure and potassium ferrocyanide were not taken into account, assuming that they were below 1%.

Table 5- Important minerals of potassium (Patnaik, 2002).

MINERAL NAME	FORMULA	CAS NO
Carnallite	$KCl•MgCl_2•6H_2O$	1318-27-0
Feldspar	$KAlSi_3O_8$	68476-25-5
Kainite	$4KCl•4MgSO_4•11H_2O$	67145-93-1
Langbeinite	$K_2SO_4•2MgSO_4$	13826-56-7
Mica	$KH_2Al_3(SiO_4)_3$	12001-26-2
Leucite	$KAlSi_2O_6$	1302-34-7
Leunite	$K_2SO_4•MgSO_4•4H_2O$	15226-80-9
Polyhalite	$K_2SO_4•MgSO_4•2CaSO_4•2H_2O$	15278-29-2
Sylvine	KCl	7447-40-7

type of chemical structure was formed as a result of the dissolution of the material in an alkaline environment, as II-valued cations do not dissolve in alkali.

Experiment performed; primarily for observational purposes, in a glass reactor; liquid volume kept constant at 2000 ml at a speed of 500 rpm (number of recycle per minute for mixing unit) at a temperature of 20°C with turbine mixing measurements (Da/Dt=1/3, E/Dt=1/3, Da/Dt, Da=Blade width of turbine mixer blade, Dt=Diameter of stirrer reactor, E=Height of the mixer from the bottom) in (McCabe et al., 2005). Two experiments were performed with l/s [Ratio of liquid (weight) per solid (weight)]= 5 (2000 ml/400 g sample) and 10 (200 g sample per 2000 ml). The retention time was as long as possible, but not longer than 2 hours. After 1 hour the solid phase settled to the bottom. Although the settling time is short due to the small particle size, the use of a hydrocyclone, which is suitable for separating solid particles between 5-10 microns (Sinnot, 1993), should be preferred in the pilot process stage (Figure 4).

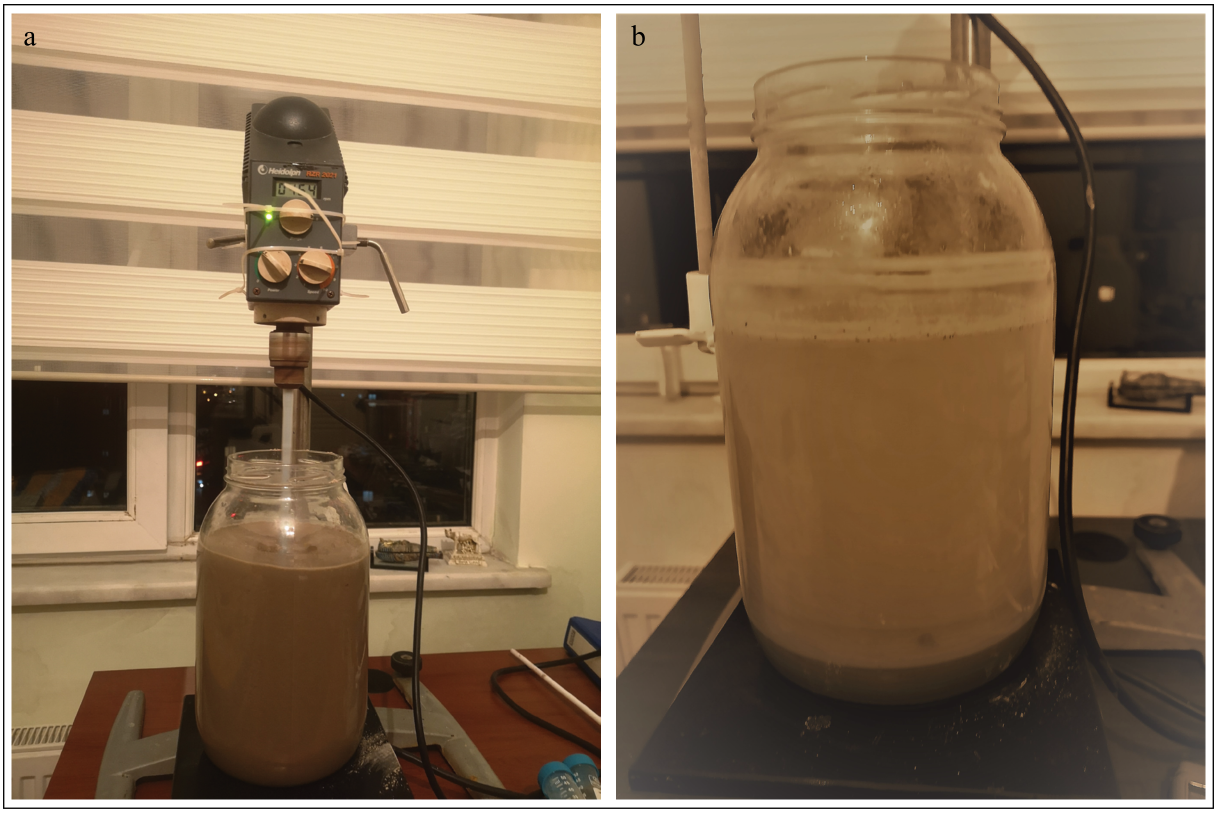

Figure 4- Laboratory studies, a) alkaline leaching studies on the material, b) resting and sedimentation phases.

In such a study, when the l/s ratio is 4, good mixing cannot be achieved below 500 rpm. It was found that 500-650 rpm is suitable.

In addition, as a final experiment, the liquid part was taken with a syringe as a result of the study carried out at 60°C with a l/s ratio of 4 (500 ml pure water/125 g material) and the solid phase (insoluble) accumulated at the bottom was washed 5 times with pure water and rested. It was dried at 105°C to observe the change in weight (Figure 5). The colour of the compounds that pass into the liquid on drying is light pink, close to the colour of natural langbeinite.

$$\eta\% = 100\ \frac{\textit{amount passing into liquid (g)}}{\textit{total ash (g)}}\ 29.85$$

29.85% was found to be obtained from volatile biomass ash.

An almost pure K_2SO_4 crystal was observed at a random point marked in SEM-EDS (Figures 6a, b and 7) according to the results of the leaching study.

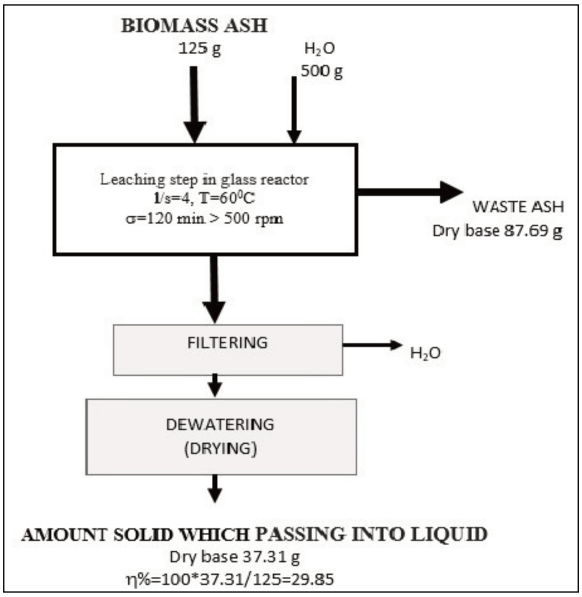

Figure 5- The leaching process.

The % gain of K: η%=100*12.49/16.84=% 74.16 for Mg, η%=100*0.03/5.41= % 0.55 has been found. The chemical composition of this structure was determined from Table 6 with acceptable elemental balance.

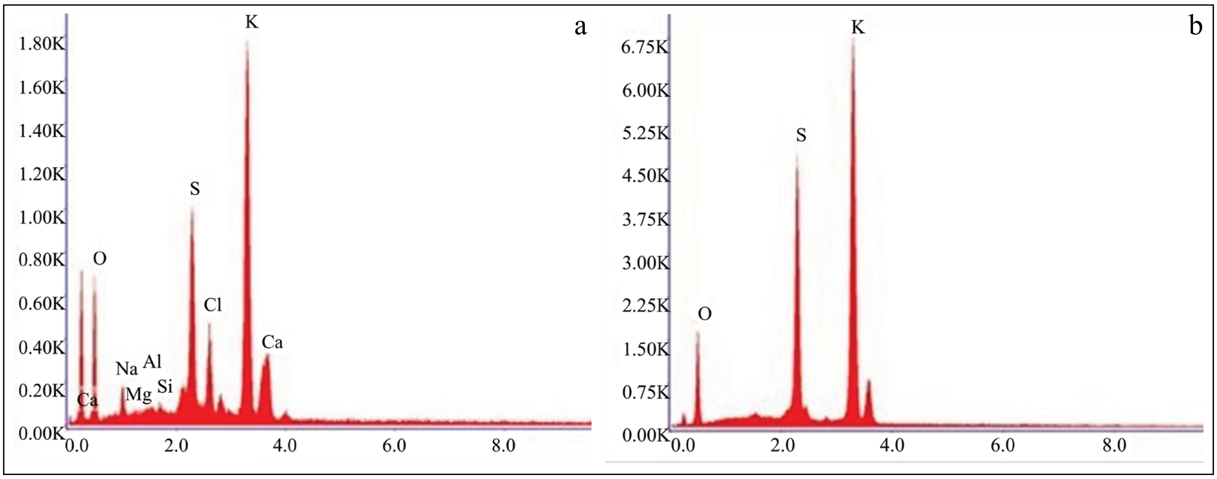

Figure 6- Peaks obtained by examination at 2 points marked in SEM (SEM-EDS). a) full area, b) clear K_2SO_4 crystal in selected or punctured full area.

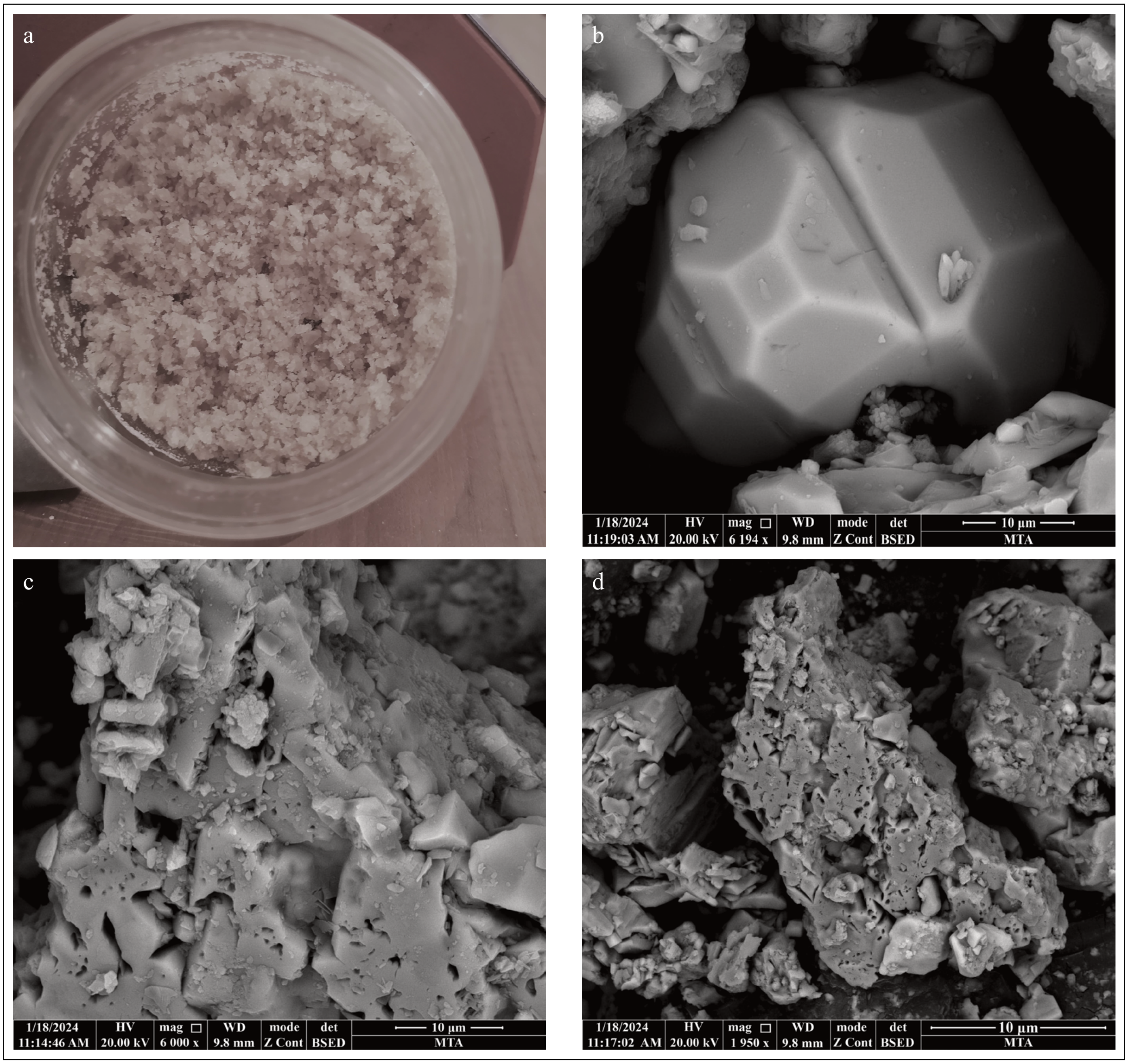

Figure 7- a) Arcanite crystals of normal size passing into the liquid part, b, c, d) Image of K_2SO_4 crystals in SEM analysis.

Table 6- ICP results and elemental balance according to gravimetric inflow and outflow in the leaching environment.

	INPUT FLY ASH (1)		**OUTPUT WASTE (2)**		**PRODUCT (3)**		
	% w/w ı cp	***In 125 (g)***	***%w/w ıcp***	***In 87.69 (g)***	***%w/w ıcp***	***In 37.31 (g)***	**(1)-(2+3) = ~0 (g)**
Al	2.00	2.50	2.80	2.46	0.05	0.02	0.03
Ca	*15.81*	*19.76*	*22.10*	*19.38*	*6.79*	*2.53*	*-2.15*
Fe	1.09	1.36	1.51	1.32	0.02	0.01	0.03
K	13.47	16.84	4.95	4.34	33.47	12.49	0.01
Mg	4.33	5.41	6.15	5.39	0.09	0.03	-0.01
Mn	0.31	0.38	0.42	0.37	0.00	0.00	0.02
Na	2.06	2.58	2.35	2.06	1.14	0.43	0.09
P	4.93	6.16	7.12	6.24	0.02	0.01	-0.09
S	6.50	8.13	2.80	2.46	15.24	5.69	-0.02
Zn	0.29	0.36	0.41	0.36	0.01	0.01	0.00

According to ICP analyses and XRF results, the main components are Ca, K, Mg, Na, Al and S, and with material balance solution, the product composition is thought to be 72.28% K_2SO_4 and also 1.23% KCl as a projection in future studies.

When the main mineral structure was examined, it was found to be aphtilide ($K_3NaO_8S_2$), sylvite ($ClK_{0,7}Na_{0.3}$), sylvine (KCl), dolomite ($CaMgO_6$-$CaMgCO_3$), $Ca(OH)_2$ and mainly arcanite (K_2SO_4). Chemical analysis was carried out at the point marked by the SEM, taken from 2 points, and a very large amount of K_2SO_4 and the visual structure (Figure 6b) are given in Table 8.

The post-leaching waste material, defined as Waste-1, was subjected to XRD analysis (Figure 8).

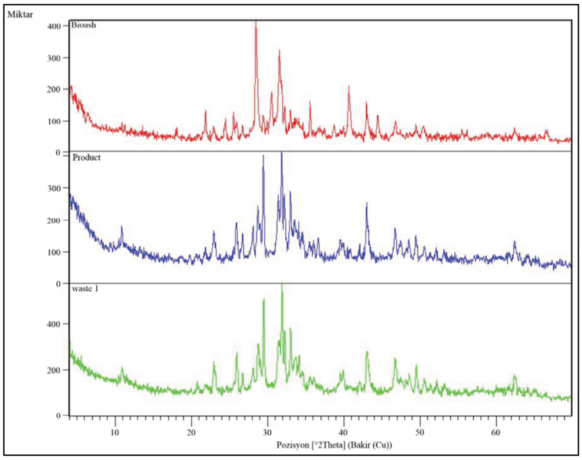

Figure 8- Detection of major minerals in the XRD analysis of the dewatered and dry solid product after leaching.

Comparative XRD diffractograms of the biomass ash (bioash), the waste and products in Figure 8. Arcanite crystals can be distinguished in the XRD diffractogram in Figure 9.

Preliminary experimental observations:

-During the study period, the pH of the liquid part was found to be 12.85. It is a highly alkaline work. In addition, a thin layer of lime cream forms on the liquid part. This is probably due to the reaction of CaO with water and $Ca(OH)_2$ in the sweat on Table 4.

-In particular, the sample with a l/s ratio of 4 was prepared at 60^{0}C with a leaching time of 120 minutes, and when the liquid solution cools to 4-5^{0}C, white crystals form at the bottom. As a result of this observation, it was concluded that it was necessary to clean this calcium-based contaminant structure.

-In the study, it was observed that when the pH was lowered to the 8.5-9 range, the solution became clear and the calcium content precipitated as black, grey crystals as

$$Ca^{2+}+SO_4^{2-} \rightarrow CaSO_4 \cong CaCl_2+H_2SO_4 \rightarrow CaSO_{4\downarrow}+2HCl\uparrow$$

were observed as possible reactions (Bayram, 2018).

When the resolution table is examined; the solubility ratio between 100^{0}C and 20^{0}C is; K_2SO_4=(24.10/7.40)=2.17, KCl=1.64, $MgSO_4$=1.79, Na_2SO_4=2.17, NaCl=1.091, $MgCl_2$=1.34 was concluded that is necessary to use the temperature

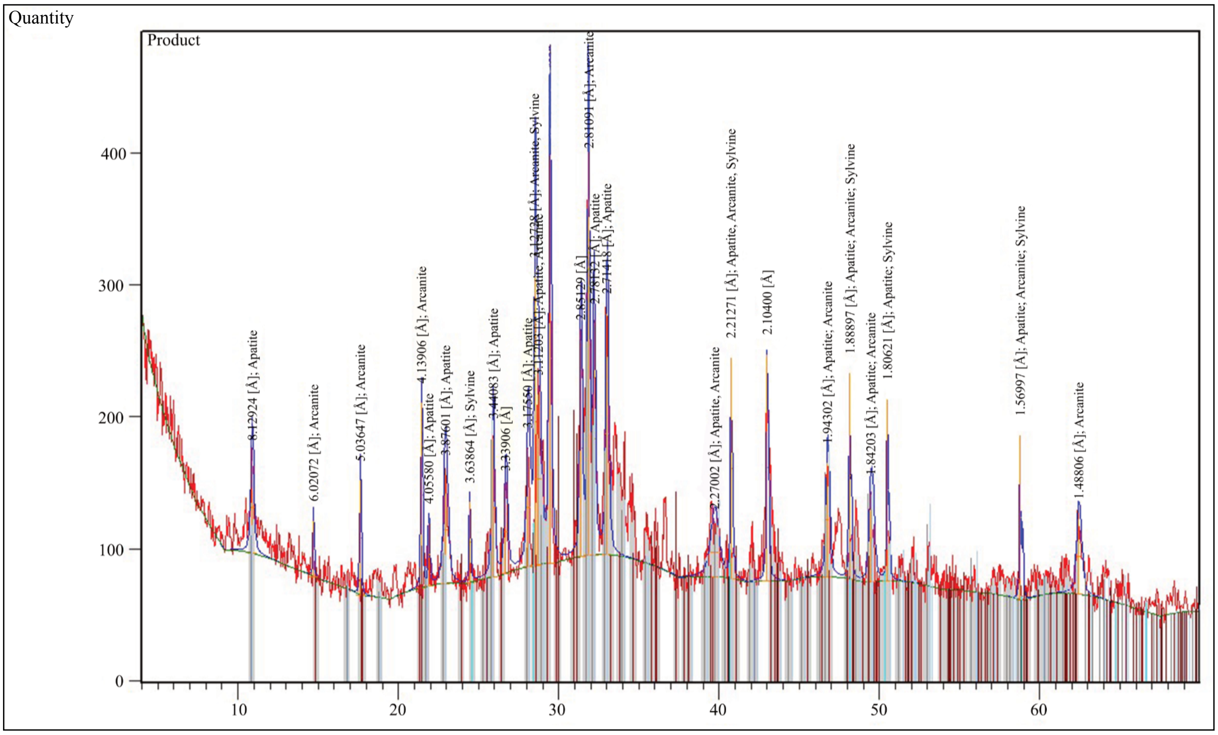

Figure 9- Detection of major minerals in the XRD analysis of the dewatered and dry solid product after leaching.

factor to reduce the l/s ratio for economic purposes. For higher solubility with less liquids, it has been found proper to operate the leaching temperature at about or close to >60°C.

4.2. Phosphorus Recovery Studies

The main chemical reactions of wet process H_3PO_4 production are given in (Becker, 1989) and are similar to the reactions according to the apatite structure.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4\downarrow + 2H_3PO_4$$

$$Ca_5(PO_4)_3(OH) + 5H_2SO_4 \rightarrow 5CaSO_4\downarrow + 3H_3PO_4 + H_2O$$

$$Ca_{10}(PO_4)_6(OH)_2 + 10H_2SO_4 \rightarrow 10CaSO_4\downarrow + 6H_3PO_4 + 2H_2O$$

Stoichiometric acid requirement per 100 grams of ash; according to the study of Krupa et al. (2008), the required amount of H_2SO_4 is given on the Table 10.

The study carried out; 40 g of 98% H_2SO_4 per 100 g was added to the material (remaining after leaching). It was well mixed with 35 g of water. The temperature of the material was rapidly increased to 100°C and the addition of 1000 ml of pure water was completed without solidification (with l/s ratio of 10) (Figure 10).

The suspended material was then mixed at a speed of 500 rpm for one hour. As a result of the one-hour rest, solid particles ($CaSO_4$+ silicates and insoluble) settled to the bottom and a direct sample was taken from the clean solution before ICP. It is the amount corresponding to H_3PO_4 over the phosphorus (P) read in the liquid.

$$H_3PO_4\ (mg/l) = reading\ (mgP/l) * (98/31)$$

The maximum that can be increased is H_3PO_4 step for H_3PO_4 production from biomass ash in the light of the studies carried out, it seems possible to produce concentrated dirty phosphoric acid in a continuous system as in Krupa et al. (2008). Only the produced samples of H_3PO_4 are taken from the system. The circulation system is H_3PO_4 solution. It seems necessary to separate $Al_2\ (SO_4)_3$ and other Mg, Na, K compounds for a cleaner phosphoric acid production.

5. Results and Discussion

-Three different processes are used in the world to produce potassium sulphate. These are the Mannheim process, the salt lake potassium sulphate process and the polyhalide (potassium chloride-magnesium sulphate)

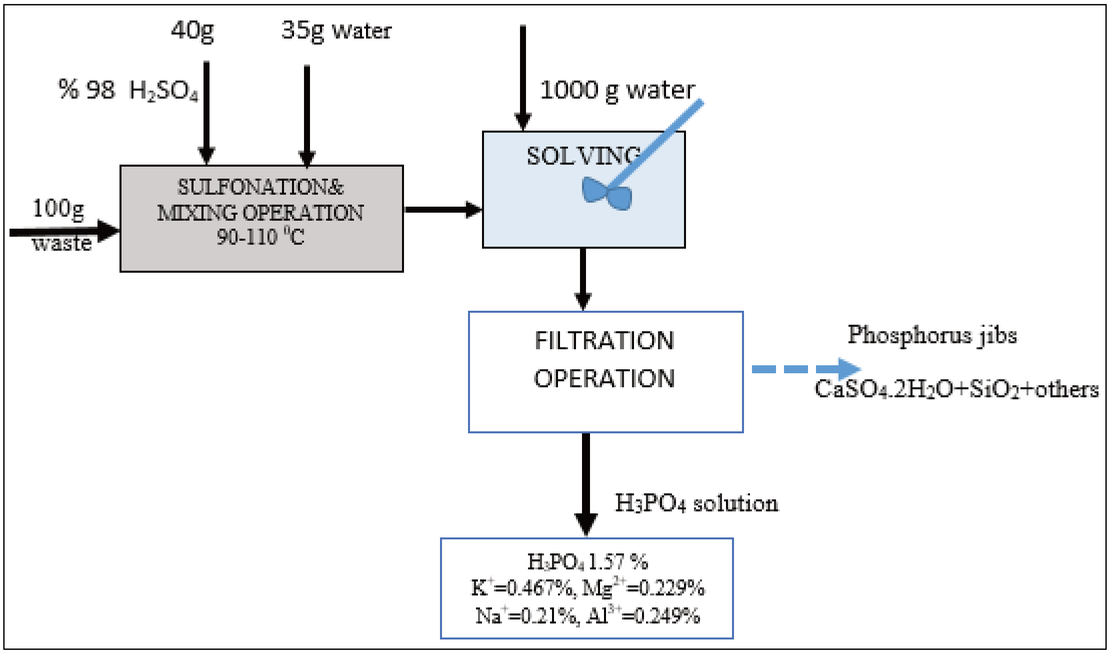

Figure 10- Suggested box-box continuation process.

potassium sulphate production process. The costs of each process are different. The process that produces the highest and best quality potassium sulphate is the Mannheim process. According to Aslan et al. (2020), depending on the process, global potassium sulphate production from saline lakes is approximately $320/tonne, $410/tonne for polyhalide and $520/tonne for KCl and H_2SO_4 using the Mannheim process.

-The largest potash producers in the world are China, Canada and Russia. Potassium sulphate production in China will increase by 8.6% between 2013 and 2018, making it the largest potassium sulphate producer. Russia already has a significant share of the potassium sulphate market. Canada has decided to invest in potassium sulphate production in recent years. The world's largest importers of potassium sulphate are Germany, Belgium and the Netherlands. These three countries account for approximately 60% of the world's total potassium sulphate imports (Aslan et al., 2020).

How this distinction can be made is illustrated by two further studies of the process.As a result of the preliminary studies;

- When the XRD analyses of the materials were examined, it was found that the langbeinite content on the fly ash was very high, but the dried material obtained at the end of the leaching process had no langbeinite content. There is a very small amount of langbeinite in the waste product.

- It has been observed that economically enriched concentrated potassium salts, which can have a market share, can be produced from biomass thermal power plant ashes by the alkaline leaching method. It is a concentrated potassium ore whose predominant structure is arcanite (K_2SO_4) with K_2O= 40.33% (pure industrial chemical K_2O is 54.02%, S=18.39%, O=36.78%) among the low temperature (even at 60°C) material.

- The reason for choosing the alkaline leaching method is that compounds such as $Mg(OH)_2$, $CaCO_3$, $MgSO_4$, $CaCl_2$ precipitate at high pH in salt water mixtures. The reason for the presence of $Ca(OH)_2$ in the current product is its alkaline nature. It is possible that this can be precipitated by the addition of H_2SO_4.

- Solid recovery: 29.85% and K recovery: 74.16%.

- The Mg recovery in the leaching process is 0.55% and this is entirely due to the high pH of the leaching process. The results are in line with our expectations.

- In addition, increasing the leaching temperature to 95-100°C and washing the remaining solids with clean solution prior to centrifugation will increase the recoveries.

- The recovery of phosphoric acid from the material by the wet process did not appear to be possible within the method followed. An alternative route should be investigated by high temperature or other studies. For example, as in Krupa et al. (2008), mixing the resulting H_3PO_4 with higher concentration clean H_3PO_4 and placing it on the market.

-The tests carried out on the waste were only designed to detect the compounds that had leached into the liquid and did not investigate the new acidic structure that could be formed by dehydration. Since only the chemical structure and the percentage composition are known, as can be seen in Table 11, the percentage H_3PO_4 can reach up to 23.76, which means that this production is not possible. Therefore, purification of the liquid composition by various alternative methods should be considered. For example, the leaching process to be carried out on the waste at pH around 7 or pH 6-7 will largely remove the K_2SO_4, $MgSO_4$, $FeSO_4$ and $Al_2(SO_4)_3$ content. However, as this process is carried out with water, it is far from being economically viable to produce due to the need for post-separation distillation etc. Nevertheless, the product is of industrial importance due to its high content.

-The resulting material is neutralized with $NH_4(OH)$ and converted into an N-P-K fertilizer.

-It has also been shown that the $MgSO_4$ and Na_2SO_4 in the material bind crystal water (Weast and Astle, 1980).

-In the light of the studies carried out, it has been seen that such a system has difficulties operating in the pH range of 11-13 in terms of corrosion and separation of materials, both theoretically and in the light of the studies carried out. Therefore, after the leaching process, the solution has to be neutralized with H_2SO_4.

$$Ca(OH)_2+H_2SO_4 \rightarrow CaSO_4.2H_2O\downarrow$$

From Table 7, theoretically H_2SO_4 requirement per 100 g biomass ash;

For $Ca(OH)_2$: 29.85* 12.25*98/(74*100)=4.84 g

More than 50% of the world's sulphate production is based on the Mannheim process.

The Mannheim process was originally developed from the production of sodium sulphate by reacting NaCl with sulphuric acid. By replacing NaCl with KCl, potassium sulphate is produced (Felton et al., 2010).

The reaction is a two-step process:

Exothermic reaction: $KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$

Endothermic reaction: $KHSO_2 + KCl \rightarrow K_2SO_4 + HCl$

Total reaction: $2KCl+H_2SO_4 \rightarrow K_2SO_4+ HCl\uparrow$
$\Delta H= 15.61$ kcal/mol

Similarly in NaCl: $2NaCl+H_2SO_4 \rightarrow Na_2SO_4+2HCl\uparrow$
$\Delta H=15.71$ kcal/mol

According to KCl: 29.85*1.23*98/ (2*74.50*100) =0.24 g

For NaCl: 29.85*1.23*98/ (2*58.5*100)=0.24 g

A total (For $Ca(OH)_2$+KCL+NaCl) of 5.32 g H_2SO_4/100 g fly ash may be required.

Maximum K_2SO_4 that can be occur: 29.85*33.47*174/(2*39*100) =22.29 g

Maximum Na_2SO_4 that can be occur: 29.85*1.23*142/(2*23*100) =1.14 g

Na_2SO_4+K_2SO_4 and the recovery of K_2SO_4 seem much easier at high temperatures (Table 9). This also means obtaining high purity K_2SO_4.

K_2SO_4 saturation at 100°C 24.10 g/100 ml water will collapse first in the tchiner-1

Na_2SO_4 saturation at 100°C 42.50 g/100 ml water

- Precipitation of some of the extracted material by neutralization with NH_4OH at a higher pH.

Alternative evaluation methods such as separation can be given as examples.

- As a result of the preliminary studies carried out

Table 7- Determination of the aproximately chemical composition of the material recovered in the liquid (K_2SO_4).

COMPONENTS	MW	MIXED MATERIAL QUANTITY	%	In 100 g material (g)							
				Ca	K	Mg	Na	S	Al	Fe	P
Al_2O_3	101.96	0.10	0.12						0.06		
$Ca(OH)_2$	74.00	10.00	**12.25**	6.62							
$CaMgO_6$	160.00	0.50	0.61	0.15		0.092					
$K_{0,7}Na_{0,3}Cl$	69.85	1.00	1.23		0.48		0.19				
$K_2Mg_2O_{12}S_3$	414.00	1.00	1.23		0.23	0.006		0.28			
K_2SO_4	***174.00***	***59.00***	***72.28***		***32.40***			***13.29***			
$K_3NaO_8S_2$	159.55	1.00	1.23		0.90		0.18	0.49			
KCl	74.50	1.00	1.23		0.64						
*Crystal-.H_2O	18	0.90	1.10								
Na_2SO_4	142.00	1.00	1.23				0.40	0.28			
NaCl	58.50	1.00	1.23				0.48				
SiO_2	60.08	5.00	6.13								
$Fe(OH)_2$	90.00	0.03	0.04							0.02	
$Ca_3(PO_4)_2$	230.00	0.10	0.12	0.02							0.01
	Σ (g)	81.63	100.00	6.81	34.65	0.10	1.24	14.34	0.06	0.02	0.01

*weight loss at 1 hour at 300°C

Note: The analyses are carried out separately with ICP and SEM-EDS and there are some differences between the analyses. This is because analyses such as Cl, O, Si cannot be carried out by ICP, SEM-EDS can accurately determine the exact result with a large number of marked points, S analyses cannot be carried out reliably by ICP and also because this study is a preliminary study prior to the project. Verification was carried out using modelling of up to 100 oxide forms to determine the structure within engineering limits of error (+-2.5%). According to the balance of 100 oxide forms Al_2O_3 0.12%, K_2O 40.34%, CaO 9.51%, SO_3 35.86%, MgO 0.13%, Na_2O 1.67%, Cl 5.06%, Fe_2O_3 0.03%, PO_4 0.04 %, volatilies 0.1%, crystals H_2O 1.1 % acceptable.

Table 8- Chemical analysis (%w/w) at the points marked with SEM-EDS.

Element	Point 1	Point 2	Average	ICP %w/w
Al		0.39	0.39	0.05
Ca		6.77	6.77	1.45
Cl		5.06	5.06	-
K	41.63	30.34	35.98	33.47
Mg		0.43	0.43	0.09
Na		4.04	4.04	1.14
O	40.09	40.52	40.31	-
S	18.28	12.04	30.32	15.24
Si		0.43	0.43	-

Table 10- The amount of H_2SO_4 required per 100 g obtaining H_3PO_4 in the material.

	%	Multiplier	Σ	
Al_2O_3	3.85	0.614	2.36	Total= 47.13 g H_2SO_4/100 g fly ash
CaO	22.13	1.479	32.73	
Fe_2O_3	1.56	0.614	0.96	
K_2O	16.23	1.041	16.90	
MgO	7.21	2.433	17.54	
Na_2O	2.77	1.582	4.38	
P_2O_5	11.29	-0.691	-7.80	
SO_3	16.25	-1.225	-19.90	

Table 9- Solubility of Na, K, Mg salts in water (% w/w) at heat [from Green and Southard (2019)].

Chemicals		0^{0}C	10^{0}C	20^{0}C	30^{0}C	40^{0}C	50^{0}C	60^{0}C	70^{0}C	80^{0}C	90^{0}C	100^{0}C
K_2SO_4	g/100 ml	7.40	9.30	11.10	13.00	14.80	16.50	18.20	19.80	21.40	22.90	24.10
KCl	g/100 ml	28.00	31.20	34.20	37.20	40.10	42.95	45.80	48.55	51.30	53.90	56.30
$MgCl_2$	g/100 ml	52.90	53.60	54.60	55.80	57.50	59.25	61.00	63.55	66.10	69.50	73.30
$MgSO_4$	g/100 ml	22.00	28.20	33.70	38.90	44.50	49.55	54.60	55.20	55.80	52.90	50.40
NaCl	g/100 ml	35.70	35.80	35.90	36.10	36.40	36.75	37.10	37.55	38.00	38.50	39.20
Na_2SO_4	g/100 ml	4.90	9.10	19.50	40.80	48.80	47.05	45.30	44.50	43.70	42.70	42.50

Table 11- The determination of the approximate liquid H_3PO_4 composition.

Element	WASTE % w/w	Expected mg/l	%	Read in ICP %w/w	liquefiable efficiency η%	Components	May occurs (g)	in liquid %	*Dry base %w/w
Al	2.8	2800	0.28	0.249	88.93	$Al_2(SO_4)_3$	22.41	2.09	**31.61**
Ca	22.1	22100	2.21	-	0.000	$CaSO_4$	-	-	-
Fe	1.51	1510	0.151	0.115	76.16	$FeSO_4$	3.12	0.29	4.0
K	4.95	4950	0.495	0.465	93.94	K_2SO_4	10.37	0.97	14.63
Mg	2.8	2800	0.28	0.229	81.79	$MgSO_4$	11.45	1.07	16.15
Na	2.35	2350	0.235	0.217	92.34	Na_2SO_4	6.70	0.63	9.45
P	7.03	7030	0.703	0.533	**75.82**	H_3PO_4	**16.85**	**1.57**	**23.76**
						H_2O	1000	93.38	0.00
						Σ	1070.90	100.00	100.00

*This calculation is for only projection purposes only and <1% Mn, Zn, Cu sulfate contents are also possible in the dry base composition.

in this study, the design process shown in Figure 11 is presented as an economic process.

- Further project work will continue in the form of key studies such as process optimisation, economisation, equipment specifications, detailed mass energy balances and determination of equipment retention times.

- This study was carried out with the resources of the MTA-Department of Mineral Analysis and Technology

(MAT) department as a preliminary study for the purpose of utilising biomass thermal power plant ashes, which have increased rapidly in our country in recent years due to the energy demand. It was carried

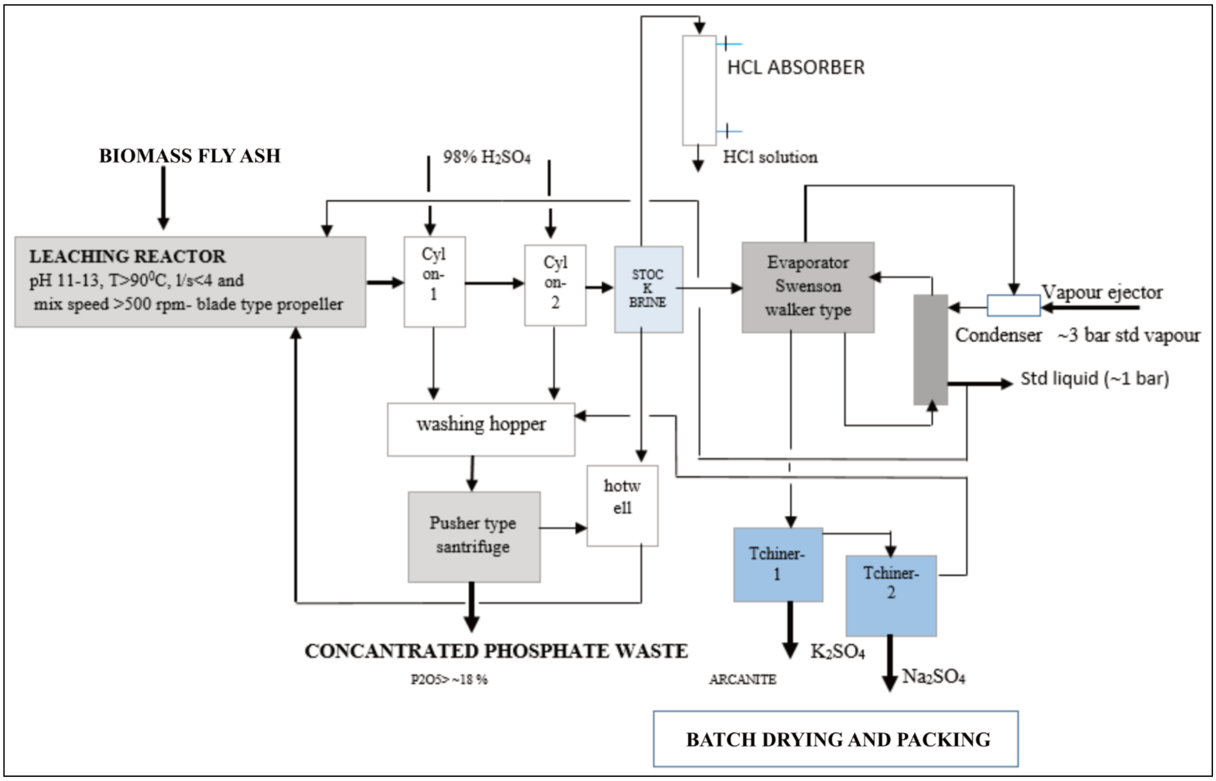

Figure 11- Suggestion draft box-box continue process step for concentrated potassium sulphate production from the biomass ash.

out only for the purpose of understanding the subject and developing a suitable method for the preliminary study of the project. Our country aims to reduce the use of potash. As far as the future waste management is concerned, the continuity of biomass ash at certain standards, the overcoming of official-bureaucratic problems in the field of the environment and the renewal of the waste management and waste disposal codes appear as an important issue for economic gain.

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