

Rare earth elements in deposited hard coal fly ash in Poland

Justyna Woźniak¹, and Marcel Gurdziel^{1,*}

¹Wrocław University of Science and Technology, Poland

Abstract. Rare Earth Elements (REEs), due to their unique properties, are nowadays a desirable raw material, especially in the development of modern technologies. This paper describes a 4-step research methodology for the task of identifying the potential for REE recovery in landfilled fly ash. A literature analysis was performed on their significance, occurrence in both primary and secondary deposits. Opportunities for REE recovery from coal fly ash in conventional power plants were identified and selected technologies were described. Poland, as a country whose energy sector is to a large extent based on coal, has a potential in this respect. Taking into account studies of the Polish Central Statistical Office (GUS) and forecasts of the Polish energy policy, the article determines the approximate value of REE in the waste stream from coal-fired power plants burning hard coal.

1 Introduction

Today's global economy relies heavily on rare earth elements. REEs are an essential raw material for the development of modern technologies, but in relation to their huge demand, their extraction is limited and it's associated with significant environmental impacts. The European Union considers REEs as a critical raw material [1] for its development with a high risk of supply interruption, as Europe is dependent on Chinese exports.

Rare Earth Elements abbreviated as REEs are a group of 17 elements, 15 from the lanthanide group plus scandium (Sc) and yttrium (Y), all of which have similar chemical and physical properties [2].

Due to their limited extraction, more and more countries are beginning to look more favorably at the possibility of extracting REE from secondary deposits. Fly ash from coal combustion is an industrial waste with high recovery potential. Interest in REE recovery from fly ash continues to grow. Perhaps in the future, countries without natural occurrences of REE ores will be able to extract these elements using waste heaps they have previously created.

2 Research Methodology

The research tasks include verification of current knowledge and conducted research in the field of national and international possibilities of REE recovery in the activity of coal-fired

* Corresponding author: marcelgurdziel@gmail.com

The coming decades should focus on the development of technologies that will be able to cope with the growing environmental pollution. In order to achieve this, a change in attitude towards the waste we produce is required, as even though it is considered a reject, it often contains many useful components that can be reused. This is especially true for materials whose natural occurrence is limited.

A waste that has attracted the attention of many researchers because of its REE content is the fly ash produced during coal combustion. The REE content of coal is related to the presence of impurities in the form of clay minerals. Hard coal and lignite have different REE contents due to the region they come from, with hard coal having a significantly higher REE content.

4 Coal combustion products, fly ash

When coal is burned in a power plant, the combustion gases escape from the chimneys in the form of gases, while the impurities contained in the coal together with the remains of the unburned coal remain in the combustion site as a solid fraction. During the combustion process, rare earth compounds pass from the coal to the ash, binding with the glassy fraction formed in the process. As a result, the content of REEs and other valuable metals in combustion products is many times higher than in coal itself. Of all coal combustion products, the highest REE content is found in fly ash.

Coal in the deposit contains a cross section of many elements in low concentrations. As shown in the study [5], fly ash collected from 10 Polish hard coal-fired power plants showed a content of 53 elements, a considerable part of which are the elements included in the list of critical raw materials [1]: cobalt (Co), tungsten (W), titanium (Ti), lithium (Li). Among the valuable metals contained in the material, rare earth elements can boast a large representation.

As can be read in [6] in Poland in 2019, the industry produced 115.3 million tons of waste, of which 2.1% was coal fly ash. It follows that the Polish coal-related industry produced 2.5 million tons of fly ash this year. According to [7] in 2019, 78.6 million tons of coal combustion byproducts were produced in the United States, of which 29.3 million tons were fly ash, 17.8 million tons of fly ash produced were reused.

5 Potential recovery of RRE from coal fly ash

The study of [8] shows that the recovery of REE from fly ash can be challenging due to the presence of a dominant amorphous fraction, whose solution requires strong acidic conditions. Fly ash particles can be considered as spherical structures made of amorphous phase that bind REEs in their interior, due to this structure during the recovery, it is necessary to create conditions in the solution so that the acid ions can act on the particles containing rare earth elements on as much of their surface as possible. This will result in the passage of a large mass of REE compounds into solution, and this means a high recovery of the desired metals.

The structure of fly ash is complex and requires careful study before conducting recovery operations. In order to achieve satisfactory results in terms of both REE yield and economic viability, it is necessary to thoroughly understand the implications that each process step will have on the material under study.

The most widely used method of conducting REE recovery on fly ash is leaching, this process involves treating the test material with a suitable liquid. As a result of the leaching process, specific compounds contained in the solid under the influence of the surrounding liquid will begin to migrate into it. In the case of REE recovery, they are the material against which it is desired to move into the liquid. In contrast, the liquid that stimulates the transition process is various acids, including hydrochloric acid and sulfuric acid [9].

As evidenced by many studies, leaching extraction of raw ash does not give satisfactory results. In order to increase the amount of REEs recovered, before leaching the ash goes through other technological processes to increase the susceptibility of the material to leaching. Test results show that REEs associated with the amorphous fraction are difficult to extract. For this reason, various processes are carried out to allow the acids to act on the glassy structures prior to leaching.

6 Results

In Poland, coal fly ash has the greatest chance of becoming a source of rare earth elements in the future due to its mass potential. As it can be read in [6], 1.8 million tons of coal fly ash were produced in Poland in 2018. Assuming that the average REE content in Polish fly ash is about 280 ppm [10], so in 2018, 504 tons of rare earths were produced in Poland, which were not recovered in any way, and some of them ended up in heaps. This is a certain assumption bearing in mind that not all of the metals contained in the ash will be recovered, how much of them will be extracted depends on the recovery method that will be used. Currently applied methods give different results, allowing recovery of either 90% or 40%. Which of the currently tested methods will be used on an industrial scale in the future depends on the profitability of its application.

However, if currently half of the annually produced REEs could be economically recovered, Poland would join the world's leading producers of these metals [11]. Poland seems to be a country which has a great potential to become a producer of REE from coal ashes in the future.

The literature analysis allowed to indicate the averaged REE content in Polish fly ash. Using statistical data (environment and energy scope) on waste management [6, 12, 13, 14, 15, 16, 17], a rough analysis of REE recovery potential in Poland was performed. These data refer to coal fly ash, without division into lignite or hard coal (Table 1). Moreover, the fly ash stored so far represents a research potential towards REE, among others.

Tab. 1. Fly ash - summary 2015 - 2020 Source: own elaboration based on [12].

Year	Coal fly ash [million tonnes]	Storage to date [million tonnes]
2015	3.84	26.86
2016	3.28	26.28
2017	3.26	25.98
2018	3.41	25.27
2019	2.42	25.54
2020	1.93	25.01

Analysis of the bibliography indicated that coal fly ash was the source of REE occurrence. Using the country's electricity balance sheet [18] and the share of carriers in electricity generation (Tab. 2), the proportional share of coal fly ash was determined (Table 3).

Tab. 2. Share of coal in electricity production [GWh]. Source: based on GUS and assumptions of the energy policy.

Year	Hard coal		Lignite		Total	Percentage of hard coal to total coal
	GWh	%	GWh	%		
2015	77693	47.38%	52825	32.21%	163994	59.53%
2016	79400	47.65%	50920	30.56%	166634	60.93%
2017	79022	46.36%	52166	30.60%	170465	60.24%
2018	81257	47.79%	49331	29.01%	170039	62.22%
2019	76539	46.67%	49331	30.08%	163989	60.81%
2020	72800	45.16%	48300	29.96%	161200	60.12%
2025	68200	39.42%	48300	27.92%	173000	58.54%
2030	66800	35.63%	43600	23.25%	187500	60.51%

The data for 2015-2019 came from the Polish Central Statistical Office (GUS), while for 2020 - 2025 - 2030 (in a 5-year interval), are projections from Appendix 2 of the ministerial document Energy Policy of Poland [19].

Assuming an average REE content of 280 ppm in Polish fly ash [10], approximate REE calculations were performed for individual years taking into account forecast assumptions until 2030. The average value is approximately 424 tons of REE (Table 3).

Tab. 3: Estimated national REE recovery. Source: study based on GUS and energy policy forecasts.

Year	Coal fly ash [million tons]	Hard coal ash [million tons]	REE [tons]
2015	3.84	2.28	639.33
2016	3.28	2.00	559.86
2017	3.26	1.96	549.49
2018	3.41	2.12	594.81
2019	2.42	1.47	412.26
2020	1.93	1.16	324.70

2025	1.25	0.73	204.89
2030	0.65	0.39	110.12
mean			424.43

7 Summary

Literature analysis showed that the study of REE recovery from coal fly ash is a fairly new issue, and its results are presented in both percentage and ppm terms. Fly ash from coal combustion was assumed as representative. Additionally, assuming an average REE value in Polish fly ash, an approximate value of these elements was calculated for the annual stream, with a forecast to 2030. The abundance of fly ash stored to date was indicated.

The results of this work shed new light on the recovery of rare earth elements in both international and national contexts. Research in this field is growing rapidly, and Poland may benefit in the future from the annually produced waste generated by energy plants.

In the coming years, mankind must begin to take decisive action to reduce environmental degradation. One of these actions can be recycling of industrial waste. Efforts of scientists all over the world make the knowledge about the recovery of elements constantly increasing. Thanks to their work it will be possible in the future to build an industry that will provide us with necessary materials without worsening the condition of the environment, making it a friendly home for all its inhabitants.

8 References

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