

Computational Results of the Ecotoxic Analysis of Fly and Bottom Ash from Oil Shale Power Plants and Shale Oil Production Facilities

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In Estonia, oil shale ash was considered as hazardous waste until the end of 2019 mainly due to its high content of calcium oxide. This limited the use and export of the produced ash. During 2018 and 2019, a study on the overall hazardous potential of Estonian oil shale ash was conducted. In this paper, we present the computational ecotoxic analysis results of fly and bottom ash from oil shale power plants and shale oil production plants. According to recommendations by the European Commission, computational methods are preferred for the evaluation of ecotoxicity. These methods take into account the concentrations of environmentally hazardous compounds. In order to evaluate ecotoxicity in light of hazardous property 14 (HP14, Ecotoxic), 14 different types of fly and bottom ash samples were collected and their trace element concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectroscopy (XRF). This enabled analysing all major ash streams of the Estonian oil shale industry. In turn, the toxicity values were calculated according to European Union regulations. The results showed that oil shale ash samples should not be considered as hazardous regarding HP14 – the resulting summed concentrations remained around ten times under the limit values for all four different calculation methods. For example, the highest result was 3.918 % (for a limit value of 25 %), indicating the low concentrations of hazardous elements in the investigated material. As a result, oil shale ash, similarly to coal ash, is not considered to be hazardous as of the beginning of 2020.

1. Introduction

As described by the European Commission, the properties of hazardous wastes are described using 15 hazardous property codes (HP1-HP15). A substance is considered to be hazardous if it displays one or more of these properties. Examples of these properties include explosivity, flammability, oxidising properties, etc. Ecotoxicity is described as the property of presenting immediate or delayed risks for one or more sectors of the environment. The list of waste established by the European Commission in 2000 did not contain a separate waste code for oil shale ash (European Commission, 2000). However, there were specific codes assigned to waste produced in power stations and other combustion plants. Most of the latter were considered as non-hazardous.

During the conversion of fossil fuels to energy, vast amounts of solid wastes are produced. In Estonia, about 8 Mt of alkaline ash are being produced during the thermal treatment of oil shale annually (Pihu et al., 2019). The alkalinity of the ash results from the high content of total calcium oxide in the ash – for circulating fluidised bed combustion (CFBC) technology ash samples the free CaO content is up to 10 % (Pihu et al., 2019). In Estonia, oil shale ash was considered to be hazardous waste until the end of 2019. This meant that the recycling potential of oil shale ash was limited due to its properties. There are numerous examples of how oil shale ash could be beneficially utilised – some examples include its use as a soil remediating agent (Triisberg-Uljas et al., 2018), as a road subgrade material (Wei et al., 2019), or as an adsorption material (Al-Qodah, 2000). Additionally, the classification of waste has a considerable impact on oil shale industry – when oil shale ash is not considered as harmful waste, its use and handling would be simplified. In the last years the reuse of oil shale was highly limited and in that economical environment only about 2 % of the produced oil shale ash was recycled (Estonian Ministry of the Environment, 2019). During thermal treatment, ash is produced as two main streams – bottom

ash in the furnace and fly ash as ash from economiser, electrostatic precipitator, etc. However, in this paper, all of the fly ash samples are analysed separately, so that if even one of the streams would not exhibit hazardous properties, it could be potentially used for recycling.

As oil shale ash is currently mostly landfilled in Estonia, since it was considered as hazardous waste. Ash could be part of circular economy. In the years 2018-2019 a study was conducted in which all of the hazardous properties of several oil shale samples were investigated. This paper focused on one of these properties – ecotoxicity. According to legislation by the Directorate General of the Environment of the European Commission, the most suitable method for the evaluation of HP14 is the computational method, which takes into account the composition of the investigated material. A specific method for the assessment of ecotoxic properties was provided in the EU regulation 2017/997 (The European Parliament and the Council of the European Union, 2017). This regulation also states that member states are obliged to follow the guidelines of their own countries for the assessment (The European Parliament and the Council of the European Union, 2008a). The use of computational methods presumes that the composition of the investigated waste material is well characterised – all of the ecotoxic components' concentrations must be analysed, quantified and classified in accordance with the CLP (Classification, Labelling and Packaging) directive. So far, no single validated test method is available in Europe, and computational methods are used. To the best of the authors' knowledge, there is no relevant data reported about the ecotoxicity of large scale Estonian oil shale industry ash samples. The aim of this paper was to fill the gap – compare and offer the computational results of ecotoxicity for all different oil shale ash samples produced in the Estonian oil shale industry, from major power and oil production facilities.

2. Experimental

2.1 Sample collection and analysis

The samples were gathered from five industrial facilities using oil shale as fuel. These were two different CFBC facilities (Auvere and Eesti power plant, CFBC Auvere and CFBC EEJ), a pulverised combustion facility equipped with a novel integrated desulphurization equipment (PC-NID), Petroter facility (solid heat carrier technology) and Kiviter facility (Viru Keemia Grupp, gaseous heat carrier technology). For the CFBC facilities the following ash samples were collected – bottom (BA), economiser (ECO), air preheater (APH) and ashes from four-field electrostatic precipitator (ESP1-4). In case of Auvere, a fifth ESP field (ESP5) ash and one fabric filter (FF) ash sample were also collected. For the PC-NID facility bottom, superheater (SH), economiser, cyclon (CYC) and NID ash samples were gathered. The descriptions of the technologies can be found elsewhere, namely – applied to the ash landfill in Kohtla-Järve Estonia (Vallner et al., 2015), ash cementation properties (Pihu et al., 2012) and fluidized-bed boiler in Narva thermal power plants (Bitjukova et al., 2010).

The samples can be divided into two – bottom ash (BA) and fly ash (FA, all the other samples except bottom ash). For Kiviter and Petroter only general ash samples were collected. This resulted in 14 different types of samples, which generated all-in-all 23 samples. The choice of samples covered all the major ash streams of Estonian oil shale industry. The ash samples were dried and crushed to analytical size and analysed according to local standards. Trace elements were quantified using inductively coupled plasma mass spectrometry (ICP-MS) – Thermo iCAP Qc Quadrupole and wavelength dispersive X-ray fluorescence spectroscopy with a Rigaku ZSX Primus II 4 kW. The average relative standard deviation for all measurements remained under 3 %.

2.2 Description of calculation methods

As stated by the European Union, the following equations (1-4) are used for the calculation of HP14 (The European Parliament and the Council of the European Union, 2017):

$$A: c(H420) \geq 0.1 \%, \text{ or } B: \sum(c H400 \geq 25 \%, \text{ or } C: (100 \times \sum(c H410) + (10 \times \sum(c H411) + (\sum c H412) \geq 25 \%, \text{ or } D: \sum c H410 + \sum c H411 + \sum c H412 + \sum c H413 \geq 25 \% \quad (1)$$

$$A: c(H420) \geq 0.1 \%, \text{ or } B: c(H400) \geq \frac{0.1}{M} \% \text{ and } \sum [c(H400) \times M] \geq 25 \%, \text{ or } C: c(H410) \geq \frac{0.1}{M} \% \text{ and } c(H411) \geq 1 \%, \text{ or } D: \sum [M \times 10 \times c(H410)] + \sum c(H411) \geq 25 \% \quad (2)$$

$$A: c(H420) \geq 0.1 \%, \text{ or } B: \sum c(H410) \geq 0.1 \%, \text{ or } C: \sum c(H411) \geq 2.5 \%, \text{ or } D: \sum c(H412) \geq 25 \%, \text{ or } E: \sum c(H413) \geq 25 \% \quad (3)$$

$$A: c(H420) \geq 0.1 \%, \text{ or } B: \sum c(H410) \geq \frac{2.5}{M} \%, \text{ or } C: \sum c(H411) \geq 2.5 \% \quad (4)$$

In all the equations c stands for concentration and \sum is the sum of the respective components. According to the European Council guidelines, the following elements compile the codes in the equations (The European Parliament and the Council of the European Union, 2008b): H400 – Zn, Cd, Hg, Cr, As, Co, Cu, Pb, Mn, Ni, Se and polyaromatic hydrocarbons (PAH); H411 – Zn, Cd, Hg, Cr, As, Cu, Pb and PAH; H411 – Ba, Ti, V, Mn, Co,

Ni, Se, Mo, Sb, Ti, Pb, Cu; H412 – Ba, Ti, V, Mn, Co, Ni, Se, Mo, Sb, Ti, Cu; H413 – Sn, Cr, V, Mo, Ba, U, Se, B, Ti, Mn, Co, Ni, Sb, Ti, Zn, Cu, Pb, Cd, Hg, As and PAH; H420 – halogenated hydrocarbons (chlorofluorohydrocarbons, methyl chloroform, etc.). If even one of the sums exceeds its respective limit value, the material will be classified as hazardous. The main components affecting the end result are the concentrations of heavy metals. For each of the components H-codes different multiplying factors (M-factors) are used depending on the element or substance. This enables very toxic and dangerous compounds to have a larger weight in the end result of a mixture. For example, elements like V, Ba and Ni have an M-factor of 1, As and Se have an M-factor of 10, PAH-s have an M-factor of 100 and Hg has an M-factor of 1,000. All of the elements used in the calculations presented in this paper had their specific M-factor values. The M-factor values in this paper were the same as suggested by Hennebert (2016). H400, H410, H411, H412 and/or H413 describe components that are harmful to the aquatic environment, namely heavy metals, the concentrations of which are the basis of this method.

3. Results and discussion

As these methods are based on summing up elements, acute and chronic cases are summed separately. According to the guidelines the elements which do not exceed the fixed concentration limits should be left out of the calculation. The calculations presented in this paper simulated the “worst case scenario” for all the ash samples. This means that all the concentrations that otherwise fall below the concentration limit were still taken into account, namely the limit of detection values were used. Although some elements may be present in both harmful and unharmed valence states (like Cr(III) and Cr(VI)), all the elements were considered to be in their most harmful state. Results for methods 1A, 3A, 4A and all of method 2 are not shown in the tables as these resulted in a sum of 0. This is due to the fact that if the concentration of the compound is well under the respective code’s limit, it should not be taken into account. Table 1 presents the results for the calculations based on methods 1 (B, C, D) and 4 (B, C).

Table 1: Ecotoxicity calculation results for methods 1 and 4, w/w %

facility	sample	1B	1C	1D	4B	4C
CFBC EEJ	BA	0.091	0.781	0.303	0.072	0.091
	FA: ECO	0.101	2.116	0.377	0.202	0.110
	FA: APH	0.099	1.689	0.364	0.160	0.107
	FA: ESP-1	0.084	2.072	0.336	0.203	0.097
	FA: ESP-2	0.071	1.797	0.299	0.178	0.085
	FA: ESP-3	0.073	2.159	0.317	0.214	0.090
	FA: ESP-4	0.070	2.155	0.296	0.213	0.084
CFBC Auvere	BA	0.121	3.830	0.344	0.378	0.089
	FA: ECO	0.086	2.666	0.280	0.266	0.074
	FA: APH	0.097	2.769	0.310	0.275	0.083
	FA: ESP-1	0.116	3.918	0.354	0.393	0.096
	FA: ESP-2	0.097	2.629	0.306	0.258	0.087
	FA: ESP-3	0.083	2.818	0.279	0.279	0.073
	FA: ESP-4	0.091	3.007	0.304	0.297	0.080
	FA: ESP-5	0.080	2.561	0.343	0.250	0.095
PC-NID	FA: FF	0.073	2.110	0.245	0.209	0.064
	BA	0.094	1.079	0.342	0.100	0.102
	FA: SH	0.081	1.256	0.314	0.120	0.092
	FA: ECO	0.085	1.230	0.323	0.116	0.096
	FA: CYC	0.095	1.490	0.364	0.140	0.108
Petroter	FA: NID	0.071	2.357	0.241	0.235	0.063
	general	0.065	2.505	0.772	0.207	0.242
Kiviter	general	0.037	1.622	0.722	0.156	0.229

The limits for method 1 were for A \geq 0.1 % and for the other three A \geq 25 %. For method 4B and 4C the limits were \geq 2.5 %. As can be seen from Table 1, even for the worst case scenario the results were significantly lower than the proposed limit values. The importance of HP14 cannot be stressed enough – this property is crucial in light of reusing ash, and its correct evaluation has a huge impact on a large part of the oil shale industry. This is also the reason behind the choice of the samples – these samples represent the major ash streams of Estonian oil shale industry.

There are numerous examples of ecotoxicity evaluation results for different materials in the literature. However, most of these include the use of laboratory experiments. For example, Tsiridis et al. have investigated the application of leaching tests for toxicity evaluation of coal fly ash and the effect of the eluates on water flea and some bacteria (Tsiridis et al., 2006). They found that the Microtox Basic Solid phase test was greatly influenced by the pH of the eluate. This is another indication of why computational methods are superior to actual laboratory tests. In light of its properties, oil shale is often compared to coal. Neufeld and Wallach showed already in 1984 that for coal fly ash leachates none of the metal concentrations exceeded the the primary drinking water standards by a factor of 100 and should not be considered hazardous (Neufeld and Wallach, 1984). Römcke, Moser and Moser showed that in case of municipal waste incineration ash samples, neither the terrestrial nor the aquatic tests showed a correlation between the biological effect and the concentration of chemicals (Römcke et al., 2009). The use of H420 has not been shown in this paper as Estonian oil shale ash samples do not contain any compounds that are hazardous to the ozone layer.

The results for the third computational method (B, C, D, E) can be seen in Table 2.

Table 2: Ecotoxicity calculation results for method 3, w/w %

facility	sample	3B	3C	3D	3E
CFBC EEJ	BA	0.007	0.091	0.089	0.116
	FA: ECO	0.020	0.110	0.104	0.143
	FA: APH	0.016	0.107	0.103	0.138
	FA: ESP-1	0.020	0.097	0.090	0.129
	FA: ESP-2	0.017	0.085	0.080	0.117
	FA: ESP-3	0.021	0.090	0.083	0.123
	FA: ESP-4	0.021	0.084	0.078	0.114
CFBC Auvere	BA	0.038	0.089	0.086	0.131
	FA: ECO	0.026	0.074	0.068	0.113
	FA: APH	0.027	0.083	0.077	0.123
	FA: ESP-1	0.038	0.096	0.088	0.132
	FA: ESP-2	0.026	0.087	0.081	0.113
	FA: ESP-3	0.028	0.073	0.066	0.112
	FA: ESP-4	0.029	0.080	0.074	0.122
	FA: ESP-5	0.025	0.095	0.090	0.134
PC-NID	FA: FF	0.021	0.064	0.060	0.100
	BA	0.010	0.102	0.101	0.130
	FA: SH	0.012	0.092	0.089	0.120
	FA: ECO	0.011	0.096	0.093	0.123
	FA: CYC	0.014	0.108	0.106	0.136
	FA: NID	0.023	0.063	0.056	0.098
Petroter	general	0.019	0.242	0.238	0.272
Kiviter	general	0.011	0.229	0.225	0.256

As can be seen from the results presented in this paper, based on computational methods, Estonian oil shale ash should not be considered hazardous as it does not exceed the limit values for none of the methods. This is somewhat to be expected as the highest concentration of an element for all the samples was titanium for Kiviter general ash sample with a concentration of 0.19 %. Most of the elemental concentrations remained in the range of 0.001 to 0.008 %. This is to be expected as hazard codes H412 and H413 mathematically do not influence the end result very much since their cumulative concentrations usually do not exceed the limit value of 25 %, as described by Hennebert (2016). This is due to the fact that concentrations of that value are unlikely to be present

in waste and that the waste would otherwise be utilised in a different manner or processed to remove valuable components. Reinik et al. (2015). have also run leaching tests on oil shale retorting residues and found that the release of selected trace elements was significantly lower than national and EU limit values

The use of computational methods for the evaluation of ecotoxicity is advised as there is no agreed upon single method how to treat different types of waste, especially when dealing with waste like fossil fuel ash. Both computational methods and methods based on leaching tests have their pros and cons. For example, computational methods have been proven to be highly sensitive to the choice of speciation and classification, which results in critical concentrations of for example Cu and Zn triggering hazardous classification. At the same time, transformations (complexation, etc.) which affect the availability of those elements are unaccounted for. Leaching tests on the other hand might underestimate the hazard of some toxic compounds and at the same time give a false positive due to some non-toxic compounds (like Ca and K, which both are major components in oil shale ash). Liquid to solid ratio and pH were found to be the most problematic factors for the leaching tests (Stiernström et al., 2016). The use of test organisms on the outcome of the ecotoxicity tests has also been discussed. Namely, as stated by Tsiridis, in order to obtain representative results, species from different levels of trophic chain should be used in order to compile a valid testing protocol (Tsiridis et al., 2012).

A computational approach similar to the one used in this paper was proposed by Cheng et al. (2019). Their approach also considers the elemental composition of the samples, calculation of a hazard score and then calculating the total score. However, they also concluded that contaminants used in their method might not accurately represent the full list of contaminants present in the investigated waste material. Additionally, for several hazardous properties the concentration data was not included, possibly leading to an over- or underestimation of the result. As described by Hennebert (2018), the use of eluates in tests with organisms might propose a problem as sometime the pH of the solution must be adjusted, resulting in the cancellation of some of the ecotoxicity. This is a good indication of how the development of a singular method that would fit samples of various compositions is very complicated.

When comparing the methods, it was noticed that method 1 yielded the highest ecotoxicity. This is due to the fact that compounds with hazard codes H410 and H411 were multiplied by factors of 10 and 100, but even in this case the sum remained well below the limit value. As oil shale and its products are often compared to coal and its products, the work of Neufeld and Wallach from 1984 should be considered – they stated that although the composition of coal conversion products varied widely, the concentrations of the metals are so low that none of them should be considered hazardous under the laws existing at that time (Neufeld and Wallach, 1984). Based on the results presented in this paper it can be concluded that ash samples from Estonian oil shale and shale oil industry do not exhibit ecotoxic properties and should not be considered as hazardous waste. However, it should be kept in mind that computational methods only account for the elemental composition of the samples. As a further development, HP14 should also be investigated using biotests and the obtained results should be compared to those of the computational methods.

4. Conclusions

This paper investigated the ecotoxic properties of 14 different types of oil shale bottom and fly ash samples from five different facilities utilising oil shale as fuel or raw material. The elemental compositions of these samples were analysed in order to calculate the ecotoxicity of the materials. Four computational methods were used instead of biological tests since according to the European Commission, computational methods are currently the most suitable. These take into account the composition of the investigated materials. Additionally, multiplication factors were used in order not to diminish the effect of very toxic and dangerous compounds. The results presented in this paper are based on the summation of different harmful compounds. For all 14 samples, none of the calculated sums exceeded the limit values, in most cases the sums were more than ten times lower than the limits. First field of electrostatic precipitator ash exhibited the highest sum, about 3.2 %, remaining well under the respective limit value for that method, 25 %. As a result, this was the first paper to analyse and show that Estonian oil shale ash samples from different facilities should not be considered as hazardous waste as for all the different ash streams, none of the four methods exhibited values over the set limit values.

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