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Accelerated Carbonation Treatment of Industrial Wastes: Physicochemical, Environmental and Economic Aspects

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Hakan Berber

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Tööstusjäätmete töötlemine kiirendatud karboniseerimismeetodil: füüsikalis-keemilised, keskkonnaalased ja majanduslikud aspektid

HAKAN BERBER

TALTECH
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Contents

List of Publications

The list of author's publications, on the basis of which the thesis has been prepared:

I **Berber H**, Frey R, Voronova V & Koroljova A (2017) A feasibility study of municipal solid waste incineration fly ash utilisation in Estonia. Waste Management & Research 35: 904–912. doi: 10.1177/0734242X17707574.

II **Berber H**, Tamm K, Leinus ML, Kuusik R & Uibu M (2019) Aggregate production from burnt oil shale and CO_2 – an Estonian perspective. Oil Shale 36: 431–447. doi: 10.3176/oil.2019.3.05.

III **Berber H**, Tamm K, Leinus ML, Kuusik R, Tõnsuaadu K, Paaver P & Uibu M (2019). Accelerated carbonation technology granulation of industrial waste: effects of mixture composition on product properties. Waste Management & Research 38: 142−155. doi: 10.1177/0734242X19886646.

Copies of these publications are included in APPENDIX A.

Other publications related to the research:

Berber H, Tamm K, Kuusik R, Hills CD, Carey PJ & Uibu M (2018) Utilization of Industrial Wastes and CO_2 in Construction Materials - an Estonian Perspective. Accelerated Carbonation for Environmental and Material Engineering Conference Program: International Conference on Accelerated Carbonation for Environmental and Material Engineering *(ACEME),* Newcastle, New South Wales, Australia, March 11-14, 2018. AIChE's Center for Energy Initiatives, 32−33.

Berber H, Tamm K, Kuusik R, Viktoria Voronova & Uibu M (2020) Accelerated carbonation technology granulation of industrial wastes: Chemical, technological and economic aspects. Estonian Economic Association (EMS) 15th Annual Conference on "Sustainable Estonia and the role of economic sciences", Tallinn, Estonia, January 23-24, 2020.

Author’s Contribution to the Publications

Contributions of the author to the papers in this thesis are:

I The author had the lead role in designing and outlining the manuscript. He was responsible for conducting analyses, interpretation of results, and manuscript preparation. He is the corresponding author.

II The author participated in planning of work. He conducted the majority of the experimental part. He was responsible for writing the manuscript and interpretation of the results. He is the corresponding author.

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Introduction

Carbon dioxide (CO_2) emissions as a type of anthropogenic greenhouse gases are a serious global environmental problem, causing climate change and threatening economic stability. Ever-increasing world energy demand has led to a significant rise in global CO_2 emissions, reaching a historic high of 33.1 Gt CO_2 in 2018 (International Energy Agency, 2018). Use of fossil fuels accounted for more than 80% of global energy consumption in 2013, while it is anticipated to still remain a primary energy source in 2050 (International Energy Agency, 2015). In addition, large amounts of hazardous industrial by-products are generated by the use of fossil fuels. Considering that social and industrial progress generally comes at an environmental price, it is of the utmost importance that the environmental burden resulting from CO_2 emissions and hazardous industrial wastes is substantially mitigated for sustainable development.

The Republic of Estonia meets its energy demand primarily by calcareous oil shale (OS), followed by natural gas, biomass, municipal solid waste (MSW) and some renewable sources. The use of OS and MSW in energy production results in significant amounts of hazardous solid wastes and CO_2 emissions. In Estonia, only 1-3% of solid wastes (OS fly and bottom ash) coming from the OS industry is recycled, with the remaining amount (approximately 7Mt) being deposited in ash fields every year (EE, 2018). Additionally, MSW incineration (MSWI) fly ash from Iru Power Plant generates another hazardous waste stream in Estonia, at an annual production of 11kt (Enefit Renewable Energy, 2017). In 2018, 11.3Mt of CO_2 were emitted from the Estonian power plants, of which OS and MSW combustion had the biggest proportion combined (Eesti Energia AS, 2018).

There is currently no treatment technology in practice for fly ashes generated at OS and MSW combustion plants in Estonia. Considering that (1) the annual energy consumption of Estonia is anticipated to increase by 5-7% in the future (Estonian Ministry of Environment, 2007), possibly resulting in even more significant hazardous waste stream and CO_2 emissions with the current energy policy; (2) by 2030, waste disposed to landfills in Estonia will have decreased by 30% (Estonian Ministry of Environment, 2007); (3) the transition of the EU from a linear to a circular economy (i.e. boosting the conversion of waste into resources as secondary raw materials) (United Nations, 2015b); (4) an anticipated increase in CO_2 emissions allowance price, specifically after the reform of the EU Emissions Trading System (Estonian Ministry of Environment, 2017); (5) the use of stringent economic instruments for environmental protection – it is crucial to develop a technologically and economically feasible solution for the utilisation of CO_2 and other industrial by-products for sustainable development. Thus, the research in this dissertation focuses on the development and applicability of novel accelerated carbonation technology accompanied with a granulation process, as a treatment and valorisation process for CO_2 emissions and hazardous industrial waste from Estonian power plants. This study addresses the waste-to-resource principle, so as to boost the use of secondary raw materials such as CO_2 and solid residues from power and cement production, which would play an important role in moving from a linear to a circular economy (CE). In general, this study would assist in achieving those targets, for instance: (1) reduction in hazardous waste disposal, as outlined in the Estonian Environmental Strategy 2030 (Estonian Ministry of Environment, 2007); (2) climate change mitigation, as planned in the Kyoto Protocol (United Nations, 1998), Paris Agreement on climate change (United Nations, 2015a), and the European Environment Policy 2050 (European

Commission, 2018); and (3) the EU becoming a world leader in CE transition, as mentioned in the Circular Economy Action Plan (European Commission, 2015).

Finally, the novelty of this doctoral work could be originated from the production of sustainable aggregates from the variety of industrial waste including OSA, MSWI ash and CKD by employing novel mixer-type granulator-based technology, which enables the conduction of hydration, carbonation and granulation steps in the same reactor.

Abbreviations

APC	Air pollution control
BA	Bottom ash
BCR	Benefit cost ratio
CAPEX	Capital expenditure
CBA	Cost & Benefit Analysis
CE	Circular economy
CFBC	Circulating fluidized bed combustion
CHP	Combined heat and power
CKD	Cement kiln dust
FGT	Flue gas treatment
GHG	Greenhouse gas
IEA	International Energy Agency
IRR	Internal rate of return
L/S	Liquid-to-solid ratio
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
NPV	Net present value
OPEX	Operational expenditure
OS	Oil shale
OSA	Oil shale ash
PF	Pulverized firing
PSD	Particle size distribution
PVC	Polyvinyl chloride
WtE	Waste-to-Energy

1. Background and Literature Review

1.1 Industrial residues

1.1.1. Municipal solid waste incineration residues

Incineration of MSW generates the following residues: (1) ash from energy recovery section (i.e. boiler ash, economiser ash); (2) residues from flue gas treatment (FGT) system (i.e. APC residues); (3) bottom ash (BA) (Joseph et al., 2018; Hjelmar et al., 2010). These ashes are collected together or separately, depending on the management option of a MSWI plant. Typically, MSWI fly ash amounts to approximately 5-15% of the total ash generated (Chandler et al., 1997), which represents around 20-30% (by weight) of the waste incinerated (Hjelmar et al., 2010).

In Europe, the number of Waste-to-Energy (WtE) plants operating in 2017 was 492. The amount of waste thermally treated in WtE plants in 2017 was around 96 Mt, resulting in a significant amount of fly ash to be handled every year (CEWEP, 2019).

MSWI fly ash needs to be carefully managed, since it is classified as a hazardous waste under code 19 01 07 in the European Waste Catalogue (European Commission, 2000) owing to its high content and leachability of heavy metals and soluble salts (Funari et al., 2017; Li et al., 2016). Table 1 shows the key components and main heavy metals of MSWI fly ash from different MSWI power plants. Since chemical composition of fly ash from the MSWI process is highly dependent on the composition of the wastes incinerated, incineration technology used, and FGT system adopted (Rendek et al., 2007), the compositions of the fly ashes originated from different plants and countries vary to some extent. Typically, CaO content in MSWI fly ash ranges between 30-40 wt.%, which gives MSWI fly ash its high alkalinity (Zhao et al., 2019). The pH value of MSWI fly ash is usually about 10-12, which can be attributed to the formation of $Ca(OH)_2$ (Dou et al., 2017). The leaching of heavy metals is greatly pH-dependent, and the degree of leaching differs among the different metals (Yakubu et al., 2018). Heavy metals such as Pb, Cr, Cu, Zn, and Cd are commonly found in MSWI fly ash (Tang et al., 2015). These heavy metals may leach into the environment in the absence of proper treatment (Pan et al., 2013). The high concentrations of Al_2O_3, Fe_2O_3 and SiO_2 in MSWI fly ash may play an important role in better physical inclusion and stability of heavy metals, since they are the main components of the cementitious materials (Sun et al., 2019). Moreover, one of the main concerns of MSWI fly ash is the high content of soluble salts (i.e. NaCl, KCl), which are the main sources of chlorine. Le Forestier and Libourel (1998) have pointed out that the high chlorine content of MSWI fly ash is primarily due to the incineration of plastics, such as polyvinyl chloride (PVC). The high concentration of chlorine in MSWI fly ash may cause a low solidification strength and high leaching rate of substances dangerous to the environment (Zhao et al., 2019; Aljerf, 2015).

Table 1. Chemical composition of MSWI fly ash

	Colangelo et al., 2015	Gunning et al., 2010	Sun et al., 2019	Zhao et al., 2019
Main constituent (wt.%)				
SiO_2	7.93	32.4	2.02	16.88
Al_2O_3	7.61	15.8	0.57	4.24
CaO	**32.11**	**32.1**	**40.80**	**33.53**
Fe_2O_3	2.03	3.4	0.42	19.37
K_2O	3.85	0.8	7.23	0.58
MgO	3.24	3.4	1.33	11.52
Na_2O	3.36	1.8	15.06	0.59
Cl	3.92	nd	27.46	10.02
Main metals (mg/kg)				
Cu	4927	4094	497	nd
Pb	3621	3003	1547	nd
Zn	4643	7778	4793	nd
Cd	62	-	124	nd
Cr	88	260	61	nd

Municipal solid waste incineration fly ashes in Estonia

In Estonia, the majority of MSW has been incinerated since 2013, when Eesti Energia AS constructed an efficient WtE unit as a new combined heat and power (CHP) unit at Iru Power Plant. Here, an efficient and up-to-date semi-dry FGT technique is used to comply with strict regulations and legislations. Solid wastes from the FGT system are collected during the removal of highly hazardous heavy metals, acids and acid precursors, and organic pollutants. In the WtE unit at Iru Power Plant, there are two types of residues other than BA: boiler ash, and solid waste residues from APC.

Boiler ash is gathered from a stack placed in the boiler, and subsequently delivered into a silo with the capacity of 75 m^3. It is kept in this silo for approximately four days. An approximate annual maximum quantity is 3.7kt. A semi-dry management system of combustion gases is used at Iru Power Plant. The APC system consists of a reactor and one baghouse filter. Solid residues are collected from both the reactor and the baghouse filter, and delivered to the residue silos with a capacity of 120 m^3. The approximate annual maximum quantity is 7.2kt.

In Estonia, there is currently no treatment technology for fly ashes generated at Iru Power Plant. As it stands, the hazardous solid residues from Iru Power Plant cannot be landfilled with its current form. It is delivered to a hazardous waste management company (Enefit Renewable Energy, 2016).

1.1.2. Oil shale ash

Oil shale (OS), as an organic-rich sedimentary rock containing kerogen, can be exploited by firing and retorting processes. The firing of keregenous OS results in large quantities of solid residues, 45-53% by weight of total OS combusted (Leben et al., 2019; Loo et al., 2018). The proportions of OS fly and bottom ashes depend on the mineral content and calorific value of the OS fired. Considering that OS is characterized as solid fuel with high mineral content and low calorific value, the proportions of bottom and fly ash could be, for instance 37% and 63% when burning low grade (8.5 MJ/kg) OS, but 30% and 70% in the case of firing upgraded (11.1 MJ/kg) OS (Plamus et al., 2011).

OS reserves are widely available in the world (e.g. USA, China, Russia, Canada, Australia, and Estonia). OS deposits are exploited only in a few countries (World Energy Council, 2016) mainly owing to the low calorific value of OS, and environmental concerns regarding its by-products.

The potential environmental impact of such by-products is highly dependent on their chemical-mineralogical compositions, which are closely related to the type of combustion/retorting processes used, and the OS utilised (Leben et al., 2019; Kuusik et al., 2012). However, the main environmental concern of oil shale ash (OSA) is attributed to large concentrations of lime, which cause highly alkaline leachates (pH 12-13). Table 2 shows the main chemical compositions of oil shale ashes sourced from different countries. The considerable amount of CaO, Al_2O_3, Fe_2O_3 and SiO_2 in OSA could be important for better physical inclusion and stability, since they are the main components of the cementitious materials.

Table 2. Chemical composition of OSA

Main constituent (wt.%)	Bai et al., 2018	Shawabkeh et al., 2004	Minster, 2013	Pihu et al., 2012
SiO_2	52.67	32.5	11.08	25.1
Al_2O_3	14.67	6.5	5.12	6.3
CaO	**12.56**	**50**	**34.10**	**45.7**
Fe_2O_3	6.48	3	2.25	4.0
K_2O	0.91	nd	0.35	2.8
MgO	2.18	3.3	0.93	5.5
Na_2O	3.47	0.5	0.21	0.2

Waste oil shale ash in Estonia

In Estonia, low grade OS is utilized by firing and retorting processes, resulting in a large number of different types of ashes. The processing of Estonian OS whose mineral matter varies between 20 and 70% results in a significant amount of solid waste, owing to its calcareous nature (Kuusik et al., 2012). Between 45–48% of Estonian OS dry matter remains as solid waste (Bauert et al., 1997). Most Estonian OS is used in power plants employing both pulverized firing (PF) and circulating fluidized bed combustion (CFBC). Oil shale ashes originated from PF and CFBC technologies are dominated by the presence of CaO content, which may vary from 26-55% in PF ash, and from 26-49% in CFBC ash (Kuusik et al., 2005; Bityukova et al., 2010).

In 2018, a total of 15.6Mt of OS was used in power and oil production, resulting in the generation of 7.2Mt of alkaline OSA. Only 1%–3% of OSA is currently utilised in construction materials or the agricultural industry, leaving about 7Mt to be deposited in ash fields every year (Eesti Energia AS, 2018). The concern associated with Estonian OSA is high free lime content, causing high alkalinity according to EU Regulation 1357/2014 (Environmental Investment Centre, 2019).

Thus, efforts have to be made to minimize the environmental impact of OS processing wastes by increasing the share of utilization, and reducing the environmental impact of the waste deposits.

1.1.3. Cement kiln dust

Cement Kiln Dust (CKD) is a fine-grained material, which is generated as a by-product in Portland cement production. CKD is generally collected from APC units (i.e. cyclones, baghouse filters, or electrostatic precipitators) at cement production plants (Maslehuddin et al., 2008; Abdel-Ghani et al., 2018). It is anticipated that cement clinker manufacturing results in large quantities of CKD, approximately 15-20% by weight of total clinker produced (Kunal and Rajor, 2012; Schorcht et al., 2013).

In 2016, the amount of CKD generated annually worldwide reached 615-820Mt, the majority of which was generally sent to landfills. The main concern associated with the disposal of waste CKD is the contamination of ground water with leachate (Kunal and Rajor, 2012).

CKD generally includes partially calcined or un-reacted raw feed, clinker dust, fuel combustion by-products, and alkali compounds and halides. The factors influencing the chemical and physical features of CKD may be the composition of the raw feed, type of cement production operation, dust collection facility, and type of fuel used (Abdel-Ghani et al., 2018). Some examples of the chemical composition of CKD from different studies are given in Table 3. Generally, CKD is an alkaline substance, which is attributed to the presence of a high concentration of lime. Therefore, the pH value of CKD is typically over 12 (Yaseri et al., 2019; Kunal and Rajor, 2012; Kunal and Rajor, 2014; Arulrajah et al., 2017). CKD contains insignificant amounts of trace metals. Therefore, metal concentrations are not typically a concern for most applications (Adaska and Taubert, 2008). The high chlorine content in CKD could be stemming from the increasing use of alternative fuels such as waste plastics as a potential replacement for some of the coal used in cement kiln manufacturing. The main objective of using alternative fuels could be to reduce the cost of fuels employed (Seo et al., 2019; Youn et al., 2019). The toxic heavy metal concentration of CKD depends on the waste fuel combusted (Kunal and Rajor, 2012). Several studies focused on reuse of CKD, for instance as an alternative to lime for soil stabilisation (Maslehuddin et al., 2008; Miller and Zaman, 2000), and as a mineral filler in asphalt concrete mixtures (Ramadan and Ashteyat, 2009). However, CKD may still contain corrosive substances such as chlorine, requiring suitable technology to mitigate its harmful nature.

Table 3. Chemical composition of CKD

Main constituent (wt.%)	Abdel-Gawwad et al. (2019)	Sharma and Goyal (2018)	Abdel-Ghani et al. (2018)	Youn et al. (2019)
SiO_2	7.31	15.00	9.47	1.52
Al_2O_3	2.36	3.2	2.48	0.23
CaO	**52.89**	**39.40**	**53.50**	**32.72**
Fe_2O_3	3.31	2.3	2.55	1.55
K_2O	5.22	3.1	3.06	35.81
MgO	0.63	1.8	1.67	0.03
Na_2O	0.95	1.4	1.83	nd
Cl	5.45	3.8	4.57	20.54

Waste cement kiln dust in Estonia

In Estonia, Kunda Nordic Tsement AS produces constructional cements and crushed limestone. The cement production process at the Kunda plant includes a wet process, in which limestone and clay are used as raw materials, accompanied by the combustion of a mixture of oil shale and petroleum coke (coal) as fuel.

The CKD remaining from the cement production process at the Kunda plant is currently disposed in a landfill. In 2018, the amount of CKD sent to landfill was around 26.7kt, which was approximately 3.7 kt less than the figure in 2017 (Kunda Nordic Tsement AS, 2019). Thus, the CKD originating in Estonia generates another substantial waste stream which, with the current handling, puts a burden on the environment.

1.1.4. Carbon dioxide emissions

The CO_2 concentration in the atmosphere has greatly risen since the pre-industrial era (Herzog et al., 2000; ESRL, 2019), which is an alarming global environmental problem. The main driver of this rapid increase has been the higher demand for energy. The latest figures indicate that global-energy related CO_2 emissions have reached a historic high of 33.1 Gt CO_2 (International Energy Agency, 2018).

Worldwide, global CO_2 emissions in different regions have shown distinctive trends since 2000 (Table 4). While EU countries and the United States have accomplished a fall in the annual CO_2 emission level in 2017 compared to 2000, China and India have experienced a steep increase in the same, also resulting in a significant increase in the worldwide CO_2 emissions.

The primary concern relating to the large amounts of global CO_2 emissions is the gradual rise in mean global temperature, as more solar radiation is trapped by the greenhouse effect (Metz et al., 2005). Global warming of the Earth consequently causes a rise in sea levels, a change in global ecology, and an increase in the frequency of natural disasters (Youn et al., 2019).

To prevent the dangerous interference of anthropogenic CO_2 emissions with the Earth's climate system, such national and global policies as the United Nations Framework Convention on Climate Change (United Nations, 1992), the Kyoto Protocol on Climate Change (United Nations, 1998), the Paris Agreement (United Nations, 2015a), Europe 2020 (European Commission, 2010), and 2050 Targets for Europe (European Commission, 2018) have been adopted. Moreover, the International Energy Agency (IEA) has introduced four different scenarios for the world's energy future: (1) The Sustainable Development Scenario; (2) The New Policies Scenario; (3) The Current Policies Scenario; and (4) The 66% 2°C Scenario (International Energy Agency, 2018). Among these scenarios, the New Policies Scenario is the central scenario of IEA, and the anticipated trends for total CO_2 emissions worldwide are given in Table 4. It is assumed that emissions worldwide continue to rise slowly until 2040, and that global temperatures may increase by at least 2.7°C by mid-century, which would not be aligned with the Paris Agreement.

Table 4. Global CO_2 emissions according to historical data and New Policies Scenario

	Total CO_2 emissions, Mt (International Energy Agency, 2018)							
						New Policies Scenario		
	2000	2003	2008	2014	2017	2025	2030	2040
Europe	4,513	4,724	4,599	3,921	4,006	3,519	3,118	2,652
United States	5,689	5,576	5,485	5,024	4,742	4,513	4,343	4,047
China	3,139	4,110	6,709	9,139	9,254	9,689	9,647	9,054
India	884,7	947,5	1,334	2,014	2,194	3,076	3,673	4,738
World	23,122	24,825	29,080	32,138	32,580	33,902	34,575	35,881

Carbon dioxide emissions in Estonia

In Estonia, the most important greenhouse gas (GHG) is CO_2. In 2017, CO_2 emissions accounted for 89.22% of total national GHG emissions, which was followed by methane (CH_4) at 5.26%, and nitrous oxide (N_2O) at 4.36% (Estonian Ministry of the Environment, 2019). In 2017, Estonia was recorded as the third highest CO_2 emitter per capita in the European Union (EU), with 16t of CO_2 equivalent per capita (Eurostat, 2019). Figure 1 shows the CO_2 emission trends by sector in Estonia from 1990 to 2017. In 2017, the emissions of CO_2 declined by 18,497kt (49.9%) compared to the figures in 1990. However, in the EU, Estonia experienced the second highest increase (+11.3%) in CO_2 emissions in 2017 compared to 2016 (Eurostat, 2018). Considering that the main driver of the CO_2 emissions in Estonia is energy-related activity, the use of OS as an energy source has been responsible for the major part of the CO_2 emissions in Estonia (Figure 2).

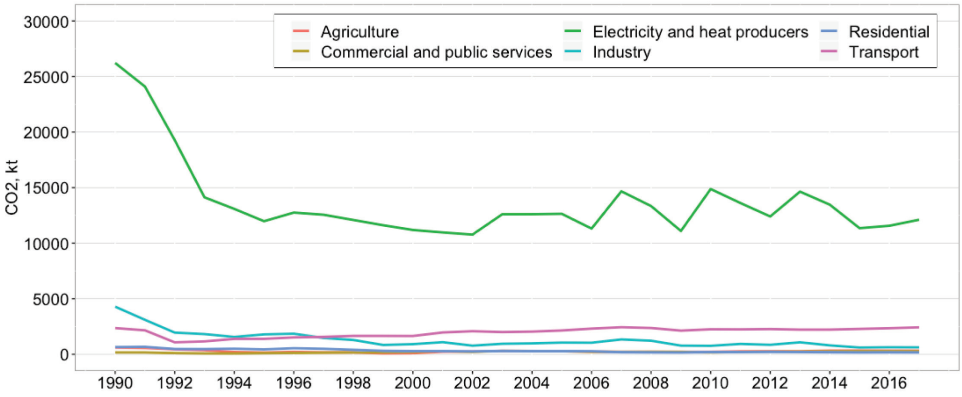

Figure 1. CO_2 emissions by sector, Estonia 1990-2017 (International Energy Agency, 2018)

To mitigate the adverse effect on climate change, Estonia has pledged to commit to the conventions mentioned above (United Nations, 1992; United Nations, 1998). Since then, Estonia provides yearly reports regarding its national anthropogenic GHG emissions by sources and removals (Estonian Ministry of the Environment, 2019). As also stated in the Estonian Environmental Strategy 2030, Estonia aims to mitigate climate change by meeting the energy demand in Estonia employing various sustainable energy production technologies, which would not have an adverse impact on the environment (Estonian Ministry of Environment, 2007).

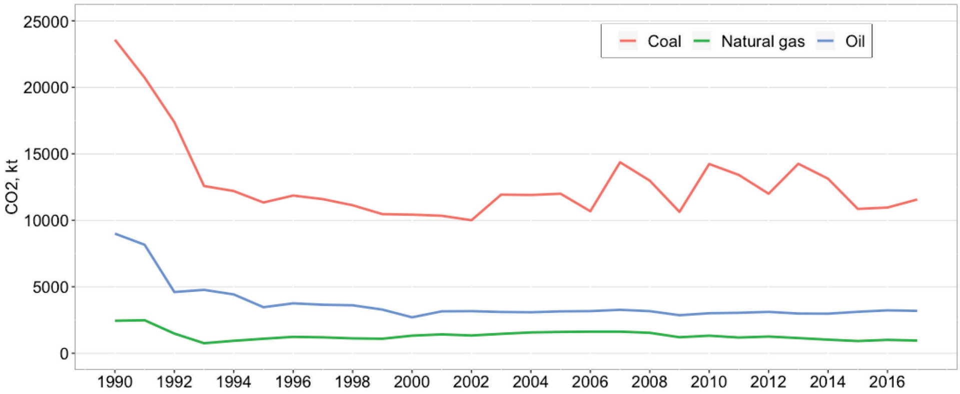

Figure 2. CO_2 emissions by energy source, Estonia 1990-2017 (International Energy Agency, 2018) (Coal stands for oil shale)

1.2. Circular economy approach

The concept of a Circular economy (CE) has gained a remarkable importance in the last decade as an attractive paradigm in order to transition towards a sustainable future (Manninen et al., 2018; Hanumante et al., 2019; Donati et al., 2020). Sustainability could overlap with the CE; nevertheless, sustainability is a driver of the CE, and mediated by innovation (Sehnem et al., 2019). Moreover, CE practices are closely related to the implementation of global Sustainable Development Goals (SDGs) as stated in the 2030 Agenda for Sustainable Development (United Nations, 2015b; Schroeder et al., 2018). In parallel, the European Commission has also adopted an EU action plan with regard to the CE, which will be instrumental in reaching the SDGs by 2030 (EC, 2015).

There are several goals to be achieved in both agendas, so as to move from a linear economy to a CE. Nevertheless, environmental sustainability is one of the most important aspects to be considered (Haupt and Hellweg, 2019). The European Commission focuses extensively on waste management and waste-to-resource principles in order to boost the use of secondary raw materials (European Commission, 2015), which also aligns with Goal 12 *“Ensure sustainable consumption and production patterns”* and Goal 13 *“Take urgent action to combat climate change and its impacts”* as within the SDGs (United Nations, 2015b).

The waste-to-resource principle is a crucial contribution to the CE approach (Pan et al., 2017). The use of concerning industrial wastes as resources – instead of employing other unfavourable management options, such as disposing into the environment – would enable environmental sustainability and circularity to be achieved by closing loops.

The Estonian government has declared that Estonia supports most of the measures in the EU’s CE action plan (Estonian Ministry of Environment, 2016). The main problematic industrial residues for Estonia were discussed in Section 1.1. Considering the lack of utilisation technologies for OSA, MSWI ashes, CKD and CO_2, it is of the utmost importance to take necessary actions in order to reach environmental sustainability and circularity in Estonia.

Table 5. Main routes to manage OSA, MSWI fly ashes and CKD

	OSA	MSWI fly ashes	CKD
Soil stabilisation	Sharo et al. (2018); Leben et al. (2017)	Show et al. (2003)	Rimal et al. (2019); Al-Homidy et al. (2019)
Stabilization/ Solidification	Reinik and Irha (2017); Leben et al. (2017); Uibu et al. (2016); Uibu et al. (2015); Qian et al. (2015)	González et al. (2017); Ye et al. (2016); Wang et al. (2010); Gunning et al. (2009)	Sharma and Goyal (2018); Huntzinger et al. (2009a); Huntzinger et al. (2009b)
Wastewater neutralization	Reinik et al. (2018b); Kindsigo et al. (2010)	-	Mahmoued et al. (2013)
Cement production	Leben et al. (2017); Nabih et al. (2014); Oymael (2007)	Lederer et al. (2017); Garcia-Lodeiro et al. (2016); Guo et al. (2015)	Maslehuddin et al. (2009)
Road construction	Reinik et al. (2018a); Leben et al. (2017)	Vehlow (2012)	Eberemu et al. (2019)
Concrete production	Leben et al. (2017); Raado et al. (2014); Smadi and Haddad (2003)	Colangelo et al. (2015)	Najim and Mahmood (2013)

There is a vast amount of different studies focusing on the treatment/utilisation of such alkaline industrial wastes. Some examples are given in Table 5. Each utilisation option has its own advantages and disadvantages, depending on the nature of the waste to be utilised. In this dissertation, accelerated carbonation technology (ACT) with/without a granulation process as a stabilisation/solidification technology was employed to utilise MSWI fly ashes, OSA, CKD and CO_2.

1.3. Mineral carbonation

CO_2 sequestration by mineral carbonation, also known as CO_2 mineral storage, is a permanent method of anthropogenic CO_2 storage without monitoring (Lackner, 2003; Li et al., 2019). Over geological timescales, the natural carbonation (natural weathering) process has played an important role in limiting the atmospheric CO_2 levels (Frondini et al., 2019). In this weathering process, alkali and alkaline earth elements such as Na, K, Ca, and Mg react with CO_2, which is dissolved in rainwater, in order to form carbonate minerals. However, this process is slow, owing to the low concentrations of CO_2 in the atmosphere (Van Ginneken et al., 2004).

Accelerated carbonation is the industrial imitation of natural carbonation. The carbonation process is accelerated by bringing reactive materials into contact with an escalated concentration of CO_2. While natural carbonation may take years or decades, the accelerated carbonation process may be completed in hours or minutes (Roy et al., 1999).

Seifritz (1990) first introduced the concept of mineral carbonation as a remedy for increasing anthropogenic CO_2 levels in the atmosphere. The relevant literature gives two main different approaches to mineral carbonation, which are direct and indirect carbonation processes (Ji and Yu, 2018). In this thesis, the focus is on the direct carbonation of waste residues.

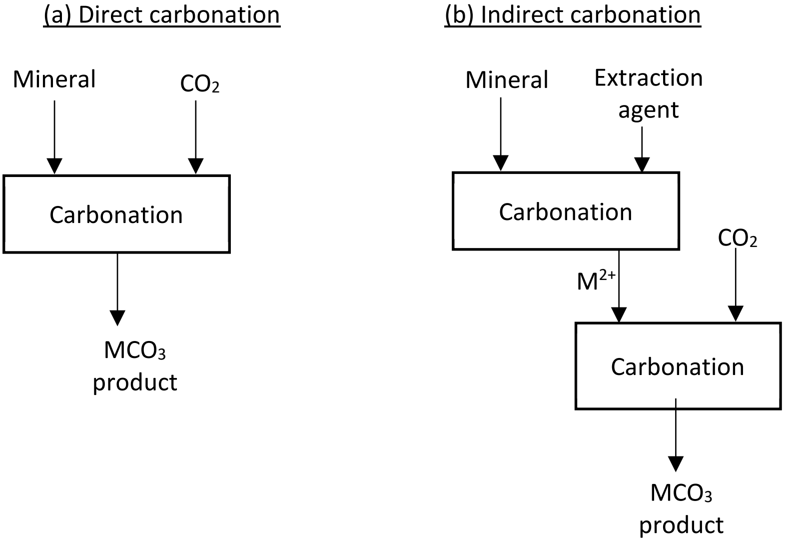

Figure 3. Schematic diagram of (a) direct aqueous carbonation process and (b) indirect carbonation process (Pan, 2015).

The main advantages of direct carbonation are its simple process design and the minimal use of chemical reagents. Direct carbonation can be divided into two types: direct gas-solid carbonation, and direct aqueous carbonation. In the aqueous carbonation route, carbonation proceeds at higher rates compared to direct gas-solid carbonation, which is perceived to be potentially sufficient for industrial implementation (Ji and Yu, 2018). The direct gas-solid carbonation route may not be an economically feasible solution, due to that this route has slow kinetics and low carbonation capacities (Mazzella et al., 2016). The superior rate of carbonation in the aqueous carbonation can be attributed to the presence of moisture, which helps separate Ca and Mg ions from the solid matrix of the carbonated material (Ji et al., 2017).

Direct aqueous carbonation of waste residues consists of three primary steps: (1) CO_2 dissolution into liquid phase; (2) metal ions leaching from the matrix of waste materials; and (3) the precipitation and crystal growth of Ca/Mg carbonates (Zevenhoven et al., 2019; Owais et al., 2019; Velts et al., 2011; Ji et al., 2017; Pan, 2015; Bauer et al., 2011; Montes-Hernandez et al., 2009). These steps can be summarised with the eq. 1-5.

$$CO_2(g) + H_2O\ (l) \rightarrow H_2CO_3(aq) \rightarrow H^+(aq) + \ HCO_3^-(aq) \tag{1}$$

$$CaO(s) + H_2O\ (l) \rightarrow Ca(OH)_2(s) \tag{2}$$

$$Ca(OH)_2(s) \rightarrow Ca^{+2}(aq) + 2OH^-(aq) \tag{3}$$

$$Ca^{+2}(aq) + CO_3^-(aq) \rightarrow CaCO_3\ (nuclei) \tag{4}$$

$$CaCO_3\ (nuclei) \rightarrow CaCO_3\ (calcite) \tag{5}$$

$$Ca\backslash Mg\ silicate\ (s) + 2H^+(aq) \rightarrow (Ca\backslash Mg)^{+2} + SiO_2(s) + \ H_2O\ (l) \tag{6}$$

$$(Ca\backslash Mg)^{+2}(aq) + HCO_3^-(aq) \rightarrow (Ca\backslash Mg)CO_3(s) + \ H^+(aq) \tag{7}$$

First, CO_2 is hydrated to form carbonic acid. Free lime in materials hydrates in water to form slaked lime. Then, calcium carbonate is formed by the reaction between calcium ions and carbonate ions. Ca and Mg elements can typically be found in silicate minerals. These minerals also have the potential to be carbonated (eq. 6-7). In principle, silica present in the mineral is exchanged with carbonate, and the mineral is carbonated.

There are several factors affecting carbonation rate and maximum carbonation efficiency:

- *Reaction time:* Increasing the time of exposure to CO_2 allows reactive waste materials to be mostly converted to calcium carbonate (Tam et al., 2005), whereas shorter reaction times could lead to poorly developed crystals (Domingo et al., 2006). However, the carbonation rate varies depending on the availability of reactive materials.
- *Temperature:* Temperature has a remarkable effect on both carbonation rate and maximum carbonation efficiency. The improved mass transfer at higher temperatures may have a positive effect on the carbonation rate in the beginning of the process. However, the fast precipitation of the Ca/Mg-carbonate products at higher temperatures may lower the carbonation rate thereafter (Ji and Yu, 2017).
- *CO_2 pressure:* The diffusion of CO_2 molecules into the solution can be enhanced with higher CO2 pressure. This allows a high concentration of dissolved CO_2 in aqua phase at high-pressure conditions, resulting in greater availability of CO_2 molecules for capture and thus a faster reaction rate (Ji et al., 2017).
- *Mineralogical and chemical composition:* Ca/Mg oxides and hydroxides in crystalline phases pose a greater carbonation rate and larger carbonation efficiency compared to silicates and alumina-silicates. Their carbonation reactivity also depends on their specific structural composition and chemical properties (Baciocchi et al., 2015; Ji et al., 2017).
- *Particle size distribution (PSD):* PSD is a key parameter largely affecting both the carbonation rate and maximum carbonation efficiency. Smaller particle size could lead to an increase in surface area of materials, which would help remove higher concentrations of metal ions from materials (Baciocchi et al., 2010). However, in very fine-grained materials, the reaction could be

inhibited owing to tighter particle packing restricting CO_2 permeation (Johnson, 2000; Zhang et al., 2004).

- *Stirring speed:* The mechanical stirring rate may increase the carbonation rate by ceasing the formation of carbonate shells covering the ash particles. Thus, the diffusion of both CO_2 and metal ions into the solution may be enhanced (Mayoral et al., 2013).
- *Liquid-to-solid ratio (L/S):* The dissolution and diffusion of both CO_2 and metal ions rely heavily on the L/S ratio. At the optimal L/S ratio, the carbonation rate is higher, due to an improved mass transfer rate (Baciocchi et al., 2010).
- Use of solvents: Solvents such as acids (acetic acid and hydrochloric acid), ammonium salts (ammonium chloride and ammonium acetate) and others (sodium citrate and water) can be used to maximise the amount of CO_2 stored (Kim and Kim, 2018; Tamm et al., 2017).

Accelerated carbonation technology (ACT) has the potential to stabilise alkaline wastes and offer long-term storage of atmospheric CO_2 (Bodor et al., 2013; Costa et al., 2007; Li et al., 2007; Seifritz, 1990). Mineral carbonation in particular is a viable option for the safe storage of CO_2 for countries whose potential for geological storage of CO_2 is close to zero (Shogenova et al., 2009).

Several studies have focused on the stabilisation of alkaline waste materials through ACT. The advantages of ACT can be stated as follows: (1) the residues show a significantly high reactivity towards CO_2, owing to the high content of lime and portlandite (Bogush et al., 2015; Huntzinger et al., 2009); (2) the alkalinity of the residues may be reduced (Astrup et al., 2006; Cappai et al., 2012; Huntzinger et al., 2009); Gunning et al., 2010; Zhang et al., 2008; Uibu et al., 2009; Velts et al., 2011); (3) the mobility of heavy metals such as lead, zinc, chromium, and copper is lowered (Baciocchi et al., 2009; Cappai et al., 2012). However, ACT may not reduce the leaching of chlorides, sulphates, or fluorides (Gunning et al., 2010). Also, contaminated solids of cementitious nature can be rapidly remediated by capsuling toxic waste into solid bulk whilst binding CO_2 in the process (Fernandez Bertos et al., 2004). The reaction products can cause rapid hardening according to equation 8:

$$CaO{\cdot}SiO_2 + yH_2O+(3 - x)CO_2\text{-}(3 - x)CaCO_3 + xCaO{\cdot}SiO_2{\cdot}yH_2O+ zCO_2\text{-}(x - z)CaO{\cdot}SiO_2{\cdot}yH_2O + zCaCO_3 \quad (8)$$

The waste residues that are discussed in Section 1.1 could be stabilised by employing ACT while permanently storing anthropogenic CO_2.

1.4. Granulation

A granulation technique, also referred as agglomeration or pelletisation, is widely used to produce artificial aggregates from a variety of industrial waste residues (Schaafsma et al., 1998; Tang and Brouwers, 2017). The granulation process is the agglomeration of moisturized fines in a rotating drum or disc to enhance bulk powder properties by grain size enlargement (Baykal and Doven, 2000).

There are several types of agglomeration methods including thermal, compression, liquid systems, and agitation (Mak, 2001). Agitation by mechanical mixing as an agglomeration technique is widely used in industrial waste utilisation (Thomas and Harilal, 2015; Colengelo et al., 2015; Gesoglu et al., 2012).

Srb and Ruzickova (1988) explain the fundamentals of the theory for this agglomeration technique. The process consists of two stages:

- *Wetting and nucleation:* To create a thin liquid film on the surface of grains, the powder material is put into contact with a liquid binder. Sufficient surface saturation leads to a nucleation process.
- *Consolidation and growth:* Wetting and nucleation enable bridges and structures to be formed between the grains. If a rotating drum or disc is used, the grains form ball-shaped structures with improved bonding forces owing to centrifugal and gravitational forces. Growth highly depends on the degree of moisturisation.

The engineering properties of the granulated products depend on several process parameters. However, it is still a challenge to predict the properties of the final products by the process parameters, due to the complex interrelationships within the process (Saleh et al., 2005).

Table 6. Some variables affecting the agglomeration process

Condition	Description
Material properties	• The fine-grained materials tend to have an enhanced granulation characteristic owing to the fact that fine-grained materials have an increased particle contact, as well as possessing an improved binder dispersion (Barnard et al., 2005; Molenaar and Venmans, 1993). However, in very fine-grained materials, the reaction could be inhibited owing to tighter particle packing restricting CO_2 permeation (Johnson, 2000; Zhang et al., 2004) • The granulation ability is promoted by the presence of a higher number of sites available in the initial material (Arandigoyen et al., 2006) • Reactivity, porosity and particle shape have an impact on agglomeration behaviour of the material (Pietsch, 2003). • Morphology and chemical properties of the material are decisive in the strength of the granules produced (Tang and Brouwers, 2017) • A solid binder applied (i.e. cement) has a significant influence on the properties of granulated products (Colengelo et al., 2015; Baykal and Doven, 2000)
Moisture content	As the amount of water injected increases, the growth rate and size of the granules increase (Arslan and Baykal, 2006). However, over-wetting may result in slurry of the material, which is not desirable for the granulation process (Litster et al., 2001)
Rotation speed	As a mechanical parameter of granulation process, higher rotation speeds enhance the magnitude of the consolidation and growth of the materials. However, extremely high rotation speeds may not result in a sufficient particle flow in the drum (Iveson, 2002)
Duration	Consolidation and growth of the grains can be enhanced by a longer agglomeration duration (Iveson, 2002)

The granulation process can be combined with accelerated carbonation to produce aggregates from industrial wastes not only to store atmospheric CO_2 for long term, but also for better stabilisation of alkaline industrial residues (Gunning et al., 2009). ACT granulation has been applied to several industrial residues to produce artificial aggregates with better engineering and environmental properties. For instance, Gunning et al. (2009) have shown that lightweight aggregates that have comparable properties to commercially available lightweight aggregates in the UK could be produced from biomass ash, CKD, MSWI FA and BA, paper ash, and wood ash. Steel slag could be also utilised by the ACT granulation process for secondary aggregate production (Morone et al., 2016; Jiang and Ling, 2020).

1.5. Decision-making approach

In project management, the decision-making framework has been intensively engaged with the strategic view of projects (Volden, 2019). The projects that are implemented are envisaged to create value and reap benefits for the parent organization, and/or society (Shenhar et al., 2001; Hjelmbrekke et al., 2017; Volden, 2019).

For effective benefit and cost management of a business case in the future, cost-benefit analysis (CBA) becomes an important part of the decision-making process (Musawir et al., 2017; Nyborg, 2014). Boardman (2015) defines CBA as *a method for assessing the economic efficiency of proposed policies or programs through the systematic prediction and valuation (i.e., monetization) of all costs and benefits to all members of society.* Conducting a forward-looking (ex ante) CBA usually requires many alternatives to be decided upon in order to achieve the same broad objective. In CBA, the resulting indicator is generally net present value (NPV). A project with the highest positive NPV is recommended to adopt among other several alternatives. Furthermore, benefit-cost ratio (BCR) and internal rate of return (IRR) are used as additional metrics (Boardman et al., 2006; Nyborg, 2014).

The benefits and costs associated with an alternative are subject to a discount rate. The main reason of discounting is that people are normally impatient, and would rather consume now than in the future. Thus, they value goods and services they consume in the future less than those they consume in the present (Boardman, 2015). Fundamentally, discount rate usage in a CBA suggests that impacts on future generations have low worth today, which is considered to be a significant weakness of the tool (Ackerman, 2004). Discount rate generally varies depending on the field in which a CBA is conducted. For instance, in a study of evaluation of electricity economics, a discount rate of 5% to 7.5% was adopted (Al-Saleh et al., 2008; Alaqeel and Suryanarayanan, 2019). Volden (2019) employed a discount rate within the range 2–5%, later fixed at 4% by analysing 58 Norwegian projects. Boardman (2015) suggests using a discount rate of 3% in a CBA pertaining to health or the environment. Therefore, in the current study, the discount rate varied within the range of 3-7%, later fixed at 4%.

CBA can be justified by two different categories, positive and normative. Positive interpretation is related to the measure of a project's efficiency, which is also closely associated with the Kaldor-Hicks compensation test. The normative justification is concerned with the improvement of social welfare through change in policy. Whilst quantification, data analysis and measurements take place in the positive interpretation, ideological, opinion-oriented, prescriptive and value judgments appear in the nucleus of the normative approach (Hammitt, 2013). In this dissertation, only the positive justification has been employed to assess the efficiency of the alternatives.

Volden (2019) proposes that there is a reasonable measurement problem in the implementation of CBA, even though the ethical and normative premises are accepted. The reason for this is that at an early stage, information about the effects of a project is sparse and depends on many assumptions; additionally, cost estimates and demand forecasts may be considerably inaccurate. Therefore, it is important to pay special attention to uncertainty estimations (Flyvbjerg, 2006).

1.6. Summary of reviewed literature and objective of the thesis

Globally, fossil fuels have been the primary energy source in the past, and are considered to play the same role in the near future. Special attention should be paid more than ever to the safe disposal of the extreme amounts of CO_2 emissions and solid waste originated from power and cement production. The global triggers behind this may be the following: (1) mitigating the adverse effects of climate change owing to the excessive amount of CO_2 emitted; (2) decreasing the detrimental impact of industrial solid waste that is disposed into the environment; (3) the use of more stringent economic instruments for environmental protection; and (4) the transition from linear economics to the CE concept (i.e. boosting the conversion of waste into resources as secondary raw materials).

In the Estonian context, there is currently no applied treatment technology for CO_2 emissions and the solid wastes (OSA, MSWI ashes, and CKD) associated with either the power or cement sectors. Considering that the Republic of Estonia has pledged its commitment to the European and international conventions relating to climate change and CE, it is of the utmost importance to provide technological solutions to enhance the current situation, while paying attention to the economic aspects of the suggested solutions.

The primary objectives of this dissertation were: (1) to theoretically study DRH carbonation technology in the treatment of MSWI ashes; (2) to focus on the development and applicability of an ACT granulation technology in producing aggregates from the previously-mentioned industrial solid wastes (MSWI ashes, OSA, and CKD) closely associated with the CE concept in light of the inventions and the targets; (3) to investigate the chemical, technological, and environmental properties of ACT granulated products; and (4) to assess the economic aspects of the both technologies.

2. Materials and Methods

2.1. Materials

2.1.2. Municipal solid waste incineration fly ash

The two types of MSWI residues investigated in this study were collected from the WtE unit at the Iru MSWI power plant in Tallinn, Estonia. The MSWI FA was gathered directly from the boiler without any treatment process applied, and the MSWI APC residues were collected from a semi-dry APC unit at the same plant. The APC system consists of a reactor and a baghouse filter, into which hydrated lime and activated carbon are injected in order to eliminate acid gases and organic pollutants. Solid residues were obtained from both the reactor and the baghouse filter, and were delivered to the residue silos in a mixed form.

2.1.3. Oil shale ash

Ash samples were gathered from different sections of the ash-separation units of the CFBC and PF boilers at the Estonian Power Plants. The BOS1 and BOS2 markers represent the ash that is produced in electrostatic precipitators, and BOS5 stands for the total ash in the circulating fluidised bed boilers of Narva Power Plant. The BOS3 sample was gathered from a pulverised firing boiler, which has a SO_2 removal system (Novel Integrated Desulphurisation, Alstom Power). The BOS4 sample was received from a shale oil production plant (Enefit280).

2.1.4. Cement kiln dust and quarry fines

The CKD, quarry fines, and ordinary Portland cement (OPC, CEM I, 42.5R) were obtained from AS Kunda Nordic Tsement in Estonia.

2.2. Methods

2.2.2. Characterization of the materials and the products

The methods in Table 7 are employed to characterise all the ash samples and some products.

Table 7. Methods for characterization of initial materials and reaction products (See ***Paper II and Paper III****)*

	Method
Chemical composition	Free CaO content using the ethylene glycol method (Reispere, 1966); Total carbon (TC) by Electra CS – 580 Carbon/Sulfur Determinator
Fractional composition	Sieving analysis (EVS-EN 933-1:2000)
Particle size distribution	Horiba LA-950 laser-scattering particle size distribution analyser
Phase composition	Quantitative X-ray diffraction (XRD) was conducted at the University of Tartu, using Bruker D8 Advanced methods, in which a scanning step of 0.02° 2θ from 2° to 75°, and a counting time of 0.5 s were used. A quantitative mineral content of powdered material was measured using the Rietveld base code Siroquant-3
Microstructure	Scanning electron microscopy and energy dispersive X-ray microanalysis methods (SEM-EDS) using a Zeiss EVO MA15 microscope with an INCA Energy 350 analyser
Elemental composition	X-ray fluorescence (XRF) spectroscopy (Rigaku Primus II) conducted at the University of Tartu, for some samples ordered from GBA Gesellschaft für Bioanalytik
Specific surface area	Kelvin 1042 sorptometer
Pore size distribution and porosity	Mercury intrusion porosimetry (MIP) using a POREMASTER-60-17 porosimeter (Quantachrome Instruments)
Compressive strength	Brookfield CT3 25K texture analyser (CEN-EN 1097-11:2013)
Density	A Mettler Toledo's density kit with universal basket for non-floating granules (EVS-EN 1097-6)
Infrared spectrum	Fourier-transform infrared spectroscopy (FTIR) spectra were recorded with a diamond crystal Bruker 55/S/NIR FTIR ATR spectrometer, at an average of 24 scans and a resolution of 4 cm-1
Environmental analysis	Leaching tests in accordance to European standard EN 12457-2:2002; The leachate pH using a Mettler Toledo SevenGo pH meter; Electrical conductivity using a Mettler Toledo SevenGo Duo Pro; Composition of selected ash leachates in accordance with DIN EN ISO 10304-1/-2(D19/20, E29); Environmental analyses using the methods of DIN EN 16171, DIN EN ISO 10523, DIN EN 27888 (C8), DIN EN ISO 17294-2 (E29), and DIN EN ISO 10304-1 D20 using GBA Gesellschaft für Bioanalytik mbH

2.2.3. Dansk Restprodukt Hantering carbonation technology

Figure 4 shows a block diagram of the Dansk Restprodukt Hantering (DRH) carbonation plant. For this plant setup, the goal is to test the process at a technical scale with continuous operation at Iru Power Plant.

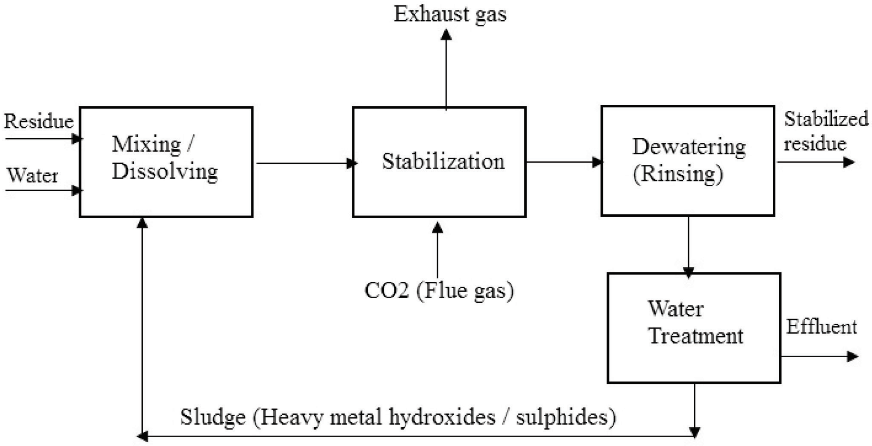

*Figure 4. Bloc diagram of the Dansk Restprodukt Hantering (DRH) carbonation process (**Paper I**)*

The mass balance for the carbonation process is shown in Figure 5. This figure is the base for the calculation of the operational cost in addition to the maintenance cost. In this DRH carbonation technology, it is first ensured that the water and FA are mixed properly. In addition, soluble salts, heavy metals and other soluble molecules are dissolved. Then, the carbonation reaction occurs where CaO reacts with CO_2. In this step, the stabilisation of FA occurs. Heavy metals are stuck in $CaCO_3$, and the alkalinity feature of FA decreases. After the rinsing process, the stabilised FA is collected. Moreover, the sludge from the wastewater treatment process is pumped back to the process. The effluent from the wastewater treatment process can be discharged into the municipal sewerage system.

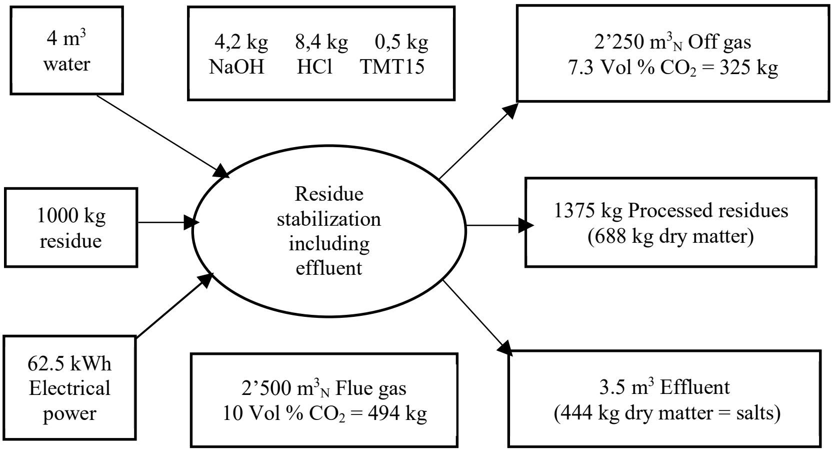

Figure 5. The mass balance of the DRH carbonation process

2.2.4. Accelerated carbonation technology combined with granulation

Figure 6 gives the experimental setup of ACT granulation. Step 1 includes premixing, hydration, and carbonation. This step is followed by combined carbonation-granulation process (Step 2). All the steps were carried out in an Eirich GmbH and Co EL1-type intensive mixer/granulator by operating under different regimes. In Step 1, the rotational speed of the rotor tool was set at 3000rmin^{-1} for intensive mixing in a clockwise direction, while in Step 2 of combined carbonation–granulation it was set at 610rmin^{-1} in an anticlockwise motion. The mixing pan was operated at a slow speed (85rmin^{-1}) throughout the experiment. First, the initial materials (200 g) were mixed with water (L/S = 0.2–0.3 w/w) for 2 min. Then, a gas flow of 20% CO_2 in air was fed into the equipment at a rate of 100L h^{-1} for 30 min. Additives, such as OPC and/or quarry fines, were added prior to Step 2. To begin the granulation process (Step 2), water was added as a liquid binder (L/S = 0.2–0.5 w/w) to initiate particle agglomeration. Once the desired granules had been formed, the gas flow of 20% CO_2 in air was led into the equipment for 20 min prior to collecting the granulated products.

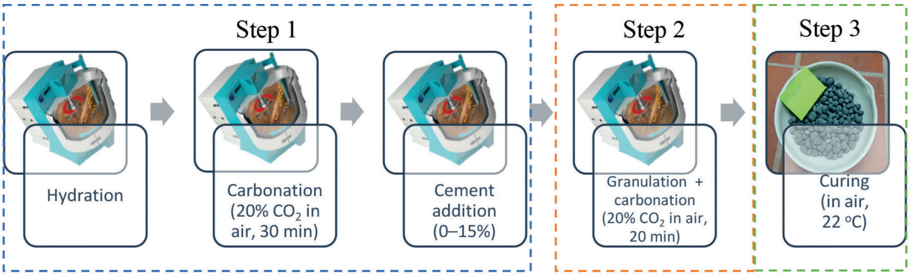

*Figure 6. ACT granulation experimental setup (**Paper II and Paper III**)*

Different mixtures were tested by ACT granulation in order to optimise the granule composition. The following methods were employed: (1) The OS ashes were solely ACT granulated except BOS4, since its fCaO content is negligible (see **Paper II-Table 2**); (2) The ratio of 1:4:1 was used to incorporate MSWI APC residue and CKD with varying OS ashes; (3) The share of MSWI ash varied between 100% and 1%. The codes of the mixtures that were used to produce granules are given in Table 8 (Q stands for 30% of quarry fines, and C stands for the portion of OPC).

The carbon dioxide binding degree ($BDCO_2$), which is considered to be one of the main indicators of carbonation efficiency, was calculated using Eq 9, where $CO_{2granules}$ is the analytically-determined CO_2 content of the granules, and CO_{2max} is the maximum possible CO_2 content of the granulated mixture of ash, OPC, and quarry fines in % according to Eq 10. CO_{2max} is calculated on the basis of total CaO content in the initial sample, where CaO_{free}^i, $CaSiO_3^i$, $Ca_2SiO_4^i$, $Ca_3Mg(SiO_4)_2^i$, $Ca_3SiO_5^i$ and $Ca_3Al_2O_6^i$ and CO_2^i are the percentages of free lime, wollastonite, belite, merwinite, alite, Ca-aluminate, and mineral CO_2 in the initial materials.

$$\mathrm{BD}_{\mathrm{CO}_2} = \frac{\mathrm{CO}_{\,2\,\mathrm{granules}}}{\mathrm{CO}_{\,2max}} \times 100, \% \qquad (9)$$

$$\mathrm{CO}_{2\max} = \frac{\frac{CaO^{i}_{free} \times M_{CO_2}}{M_{CaO}} + \frac{\mathrm{CaSiO}^{i}_{3} \times M_{CO_2}}{M_{\mathrm{CaSiO}_3}} + \frac{2Ca_2SiO^{i}_{4} \times M_{CO_2}}{M_{Ca_2SiO_4}} + \frac{3Ca_3Mg(SiO_4)^{i}_{4} \times M_{CO_2}}{M_{Ca_3Mg(SiO_4)_2}} + \frac{3Ca_3SiO^{i}_{5}}{M_{Ca_3SiO_5}} + \frac{3Ca_3Al_2O^{i}_{6}}{M_{Ca_3Al_2O_6}} + \mathrm{CO}^{\mathrm{i}}_{2}}{100 + \frac{CaO^{i}_{free} \times M_{CO_2}}{M_{CaO}} + \frac{\mathrm{CaSiO}^{i}_{3} \times M_{CO_2}}{M_{\mathrm{CaSiO}_3}} + \frac{2Ca_2SiO^{i}_{4} \times M_{CO_2}}{M_{Ca_2SiO_4}} + \frac{3Ca_3Mg(SiO_4)^{i}_{4} \times M_{CO_2}}{M_{Ca_3Mg(SiO_4)_2}} + \frac{3Ca_3SiO^{i}_{5}}{M_{Ca_3SiO_5}} + \frac{3Ca_3Al_2O^{i}_{6}}{M_{Ca_3Al_2O_6}}} \times 100 \qquad (10)$$

Table 8. The compositions of the mixtures that were used to produce granules

Mixtures	MSWI FA, %	MSWI APCr, %	BOS (1-5), %	CKD, %	Quarry fines, %	OPC, %
100APCr	-	100	-	-	-	-
95APCr/5C	-	95	-	-	-	5
65APCr:FA/Q/5C	24	41	-	-	30	5
60APCr:FA/Q/10C	22	38	-	-	30	10
1APCr:FA/94BOS1/5C	0.37	0.63	94	-	-	5
1APCr:FA/89BOS1/10C	0.37	0.63	89	-	-	10
1APCr:FA/64BOS1/Q/5C	0.37	0.63	64	-	30	5
1APCr:FA/59BOS1/Q/10C	0.37	0.63	59	-	30	10
5APCr:FA/90BOS1/5C	1.85	3.15	90	-	-	5
5APCr:FA/85BOS1/10C	1.85	3.15	85	-	-	10
5APCr:FA/60BOS1/Q/5C	1.85	3.15	60	-	30	5
5APCr:FA/55BOS1/Q/10C	1.85	3.15	55	-	30	10
95BOS1/5C	-	-	95	-	-	5
17APCr/66BOS1/17CKD	-	17	66	17	-	-
15APCr/61BOS1/15CKD/9C	-	15	61	15	-	9
11APCr/43BOS1/11CKD/Q/5C	-	11	43	11	30	5
10APCr/40BOS1/10CKD/Q/10C	-	10	40	10	30	10
95BOS2/5C	-	-	95	-	-	5
17APCr/66BOS2/17CKD	-	17	66	17	-	-
16APCr/63BOS2/16CKD/5C	-	16	63	16	-	5
15APCr/60BOS2/15CKD/10C	-	15	60	15	-	10
95BOS3/5C	-	-	95	-	-	5
14APCr/57BOS3/14CKD/15C	-	14	57	14	-	15
11APCr/43BOS3/11CKD/Q/5C	-	11	43	11	30	5
10APCr/40BOS3/10CKD/Q/10C	-	10	40	10	30	10
16APCr/63BOS4/16CKD/5C	-	16	63	16	-	5
15APCr/60BOS4/15CKD/10C	-	15	60	15	-	10
10APCr/40BOS4/10CKD/Q/10C	-	10	40	10	30	10
95BOS5/5C	-	-	95	-	-	5

2.2.5. Cost & Benefit Analysis

In a CBA, the criterion for decision-making is based on the NPV, IRR and BCR (see **Paper I** and **an additional analysis in the dissertation**). Each value is compared to those of other courses of action to determine the best option. In this equation, K refers to the initial capital investment for the first year; B and C are the benefits and costs in year t, respectively; and p_x denotes the discount rate. The discount rate varied within the range of 3-7%, later fixed at 4%.

$$NPV = -K + \sum_{t=0}^{n} \frac{B_t - C_t}{(1+p_x)^t} \tag{11}$$

The IRR is a discount rate at which a project's NPV is equal to zero. If the IRR is greater than the discount rate, the NPV is positive, which demonstrates that the project is economically feasible. The IRR is used to assess the attractiveness of a project. The formula for the IRR, as stated by Boardman et al. (2006), is given as follows:

$$0 = -K + \sum_{t=0}^{n} \frac{B_t - C_t}{(1+\pi_x)^t} \tag{12}$$

Here, π represents the IRR and the other symbols are as described as in the NPV formula.

The BCR is a ratio that should be larger than or equal to zero, which fundamentally means that the NPV of benefits is superior to that of costs to gain a profit. The general formula, as suggested by Boardman et al. (2006), is as follows:

$$BCR = \frac{\sum_{t=0}^{n} \frac{B_t}{(1+p_x)^t}}{\sum_{t=0}^{n} \frac{C_t}{(1+p_x)^t}} \tag{13}$$

3. Results and Discussions

3.1. Chemical, technological, and environmental aspects

3.1.2. Physical, chemical and phase properties of the initial materials

To understand the ability of the initial materials for carbonation and/or granulation processes, the physical, chemical and phase properties were analysed (see **Paper II** and **Paper III)**. Barnard et al. (2005) and Molenaar and Venmans (1993) have stated that fine-grained materials may have a better granulation ability, owing to enhanced particle contact and binder dispersion. In this study, MSWI APC residues, OS ashes, CKD and OPC unlike MSWI FA and quarry fines were found to be fine-grained materials (see **Paper II-Table 2,** and **Paper III-Figure 1**). This indicated that the carbonation and granulation ability of MSWI APC residues, OS ashes, CKD and OPC were relatively superior to that of MSWI FA and quarry fines. The SSA of materials used in the carbonation and/or granulation processes is one of the key characteristics, since materials with a higher number of sites available possess superior ability in the process (Arandigoyen et al., 2006). In the case of the initial materials used in the current study, MSWI FA and OPC experienced lower SSA values compared with those of MSWI APC residues, oil shale ashes and CKD (see **Paper II-Table 2,** and **Paper III-Figure 1**).

The carbonation ability of materials is generally dependent on the content of free lime and such calcium-silicates as alite, belite and merwinite, since CO_2 is captured mainly using free lime and said silicates (Uibu et al., 2009, 2011; Velts et al., 2011). In the case of OS ashes, except for the sample BOS4 that was gathered from oil production unit Enefit280, MSWI APC residues included a large amount of free lime (8-15%), whereas the amount of free lime was negligible in CKD, MSWI FA, OPC, and quarry fines. The amount of CO_2 in quarry fines was comparably higher. Quarry fines were used in the process as a filler material (see **Paper II-Table 2,** and **Paper III-Table 1**).

The result of XRD analysis indicated that calcium-silicates were present in all the residues, which would play a crucial role in capturing CO_2. The content of calcium-silicates was highest in the OS samples. As expected, MSWI ashes and CKD included a considerable amount of chlorine-bearing phases such as KCl, CaClOH and NaCl (Figure 7). The high amount of chlorine in the waste residues is one of the challenges in waste utilisation processes.

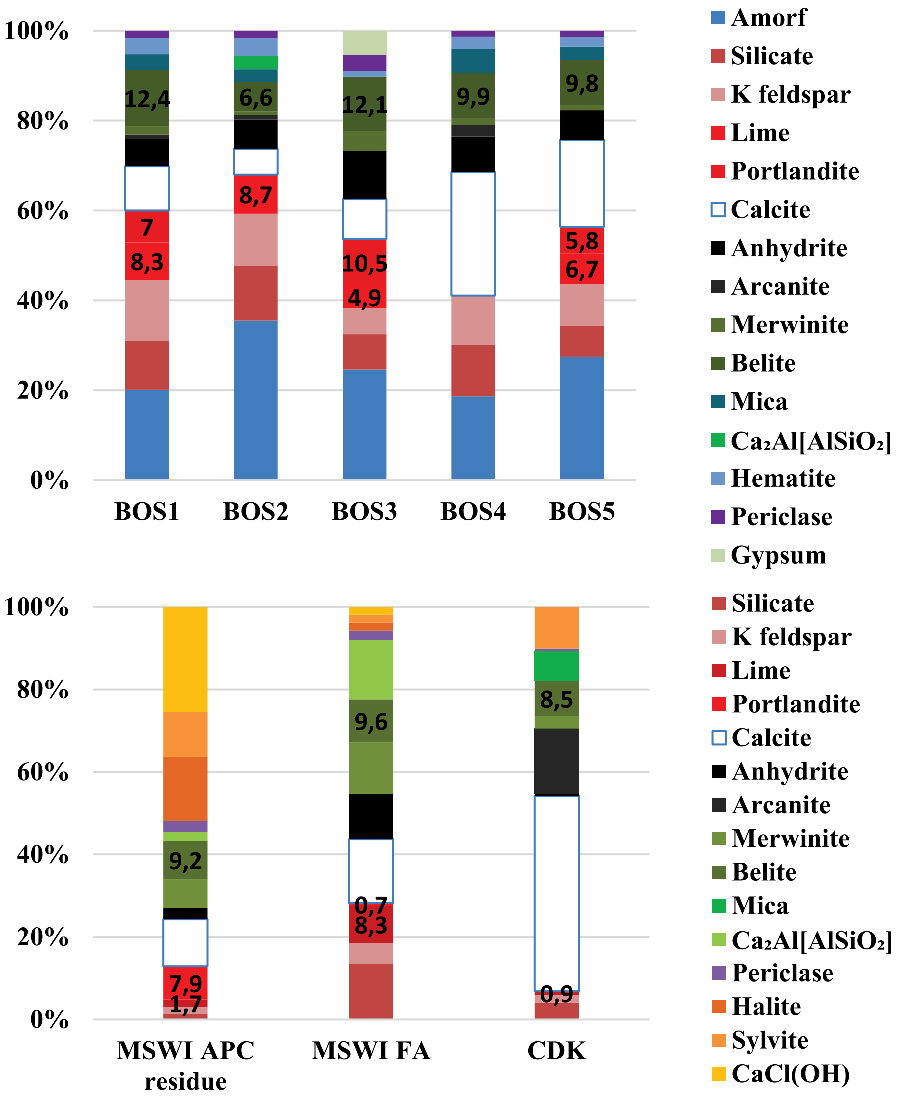

*Figure 7. Phase composition of initial materials (see **Paper II and Paper III**)*

Generally, the main challenge involved in the handling of industrial wastes is the feature of high alkalinity. In this study, the pH values of the waste ashes were significantly higher than 11.5, which is one of the requirements for inert materials (Table 9). The major concern for the OS ashes was only the high alkalinity. However, the release components of MSWI ashes and CKD also included chloride and heavy metals. The study found the most hazardous sample to be MSWI ashes (see **Paper II** and **Paper III**).

*Table 9. The release of components from initial materials ('b' refers to the limit for landfilling of inert wastes, and 'c' to the landfilling limit for hazardous wastes) (Estonian Ministry of Environment, 2004) (see **Paper II and Paper III**)*

Parameter	Limit (b)	Limit (c)	Unit	MSWI FA	MSWI APCr	CKD	BOS1
pH	6-9		-	**13.9**	**13.3**	**13.9**	**13.5**
EC			mS/cm	17.5	61.3	39.3	12.6
TDS	4	100	g/kg	**87.9**	**306**	**196**	**63.1**
Chloride	0.8	25	g/kg	**16.8**	**192.2**	**40.8**	**2.1**
Fluoride	0.01	0.5	g/kg	**0.05**	**<0.15**	**0.26**	**<0.03**
Sulphate	1	50	g/kg	**10.8**	**14.6**	**53.2**	0.016
Ca			g/kg	15.1	73.7	26.6	10.9
K			g/kg	7.1	46.6	97.8	2.8
Na			g/kg	6.6	36.4	1.7	0.1
Mg			mg/kg	<1	<1	<1	2.4
Mn			mg/kg	<0.1	<0.1	<0.1	<0.1
Hg	0.01	2	mg/kg	<0.002	**0.21**	<0.002	<0.002
Cd	0.04	5	mg/kg	0.009	<0.003	<0.003	<0.003
Pb	0.5	50	mg/kg	**4.7**	**700**	**22**	0.22
Cr	0.5	70	mg/kg	**17**	**2.6**	**4**	0.07
Ni	0.4	40	mg/kg	<0.01	<0.01	<0.01	<0.01
Zn	4	200	mg/kg	**6.2**	**130**	0.5	0.09
Cu	2	100	mg/kg	0.2	**4.1**	<0.01	<0.01
As	0.5	25	mg/kg	0.014	<0.005	0.015	<0.005
Mo	0.5	30	mg/kg	**1.8**	**4.5**	**2.5**	0.3
Ba	20	300	mg/kg	2.3	**29**	5.3	**27**

3.1.3. CO_2 binding and mechanical properties of ACT granulated wastes

To understand the behaviour of the OS ashes and MSWI APC residues in terms of CO_2 reactivity in the ACT granulation process, the waste ashes (except BOS4, that was collected from Enefit280 units) were solely carbonated in Carbonation Step 1 (Figure 6). The results showed that the carbonation reactivity of MSWI APC residues was rather lower compared to that of the OS ashes under conditions that included a low-range water-to-solid ratio (0.2–0.5 w/w) and a gas flow of 20% CO_2 in air (Figure 8). Among the OS ashes, the fCaO content remained at a higher level in the BOS3 sample, which was gathered from a PF boiler which has a SO_2 removal system. The lower BET SSA value of BOS3 may have had an adverse effect in the CO_2 uptake rate (see **Paper II-Table 2**).

The tests that were conducted to observe the changes in mean particle size and BET SSA values of MSWI APC residues and the OS ashes in Carbonation Step 1 indicated that there could be a concern for MSWI APC residues that was associated with early-stage agglomeration. This result supported the fact that carbonation reactivity of MSWI APC residues was rather lower compared to that of the OS ashes, since the agglomeration process inhibits CO_2 diffusion and the following carbonation reaction. Therefore, to achieve a higher rate of carbonation in Carbonation Step 1, the process parameters, such as L/S ratio, could be altered. It is important to note here that full carbonation of waste ashes in the first step could be detrimental to the strength development of the granulated products, since unreacted free lime acts as a potential binder by forming solid bridges in the granules (see **Paper III**).

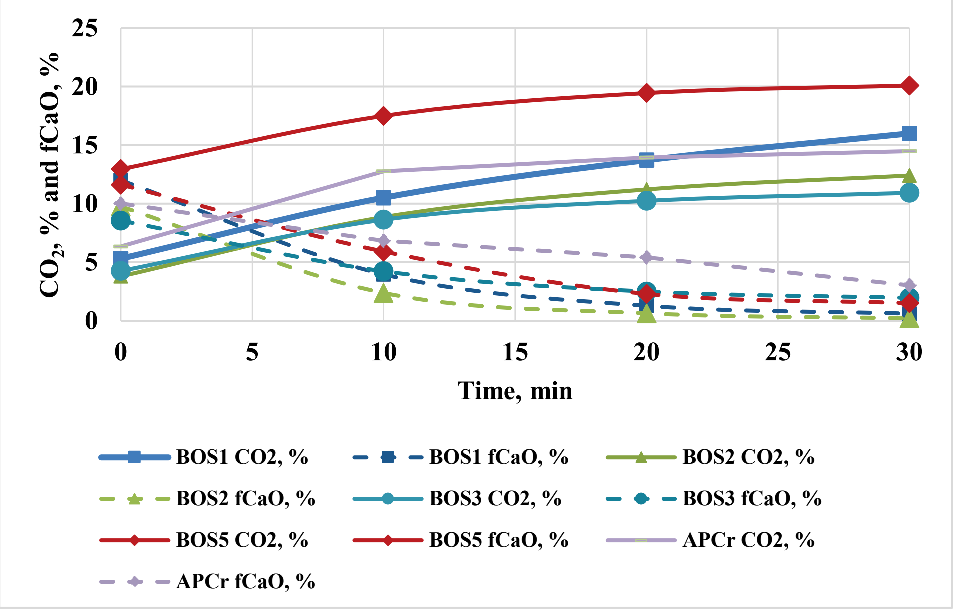

*Figure 8. Changes in CO_2 and fCaO contents in different ashes during the carbonation step (**Paper II and Paper III**)*

One of the most important properties of the granulated products is CO_2 uptake rate at the end of the process. The ACT granulated wastes experienced a range of 50%–97% for $\mathrm{BD}_{\mathrm{CO}_2}$ values, which showed that the carbonation efficiency deviated from moderate to high, depending upon the mixture's composition (Table 10). The lower $\mathrm{BD}_{\mathrm{CO}_2}$ values were obtained from the granules that included proportionally more MSWI ashes, for instance 100APCr, 95APCr/5C. The primary reason behind this finding could be early stage agglomeration (see **Paper III**).

In general, the OS-based granules possessed a moderate to high level of $\mathrm{BD}_{\mathrm{CO}_2}$ values (>70%). The addition of cement diminished the $\mathrm{BD}_{\mathrm{CO}_2}$ values. The reasons behind this fact could be owing to the following: (1) The further carbonation of the material may have been stopped because of the outer layers formed by the incorporation of cement in carbonation step 2 (Figure 6); (2) the compounds inside the cement that can be carbonated may not have been exhausted in the second carbonation step. Conversely, adding quarry fines as inert carbonates containing fillers into the mixture resulted in a comparative increase in the $\mathrm{BD}_{\mathrm{CO}_2}$ values, due to the higher proportion of carbonate content and the lower share of reactive/carbonatable content in the mixture (see **Paper II**).

In this study, the amount of CO_2 that was bound to granulated wastes ranged from 23 to 94 kg per t of waste. As the mixtures differed noticeably by the concentration of free lime and calcium-silicates, the $\mathrm{BD}_{\mathrm{CO}_2}$ and the amount of CO_2 bound per t of waste were not directly dependent on each other (Table 10).

Table 10. CO$_2$ binding characteristics and mechanical properties of ACT granulated waste (see ***Paper II and Paper III****)*

	Size distribution, %			Compressive Strength, MPa	Apparent density, g/cm^3	BD$_{CO2,}$ %	CO$_2$ bound, kg per waste t
Granules	7-10, mm	5-7, mm	4-5, mm	4-10, mm	4-10, mm	4-10, mm	4-10, mm
100APCr	58	34	1	2.88	1.75	56.49	45.62
95APCr/5C	17	50	22	3.93	1.96	49.87	39.71
65APCr:FA/Q/5C	55	28	6	3.69	2.08	74.11	54.45
60APCr:FA/Q/10C	50	35	7	2.78	2.04	61.58	23.42
1APCr:FA/94BOS1/5C	29	44	14	2.08	2.36	71.36	85.52
1APCr:FA/89BOS1/10C	52	19	5	2.17	2.37	69.87	88.31
1APCr:FA/64BOS1/Q/5C	25	48	13	1.91	2.52	82.93	67.78
1APCr:FA/59BOS1/Q/10C	25	51	15	1.82	2.47	82.02	71.67
5APCr:FA/90BOS1/5C	27	57	8	3.70	2.44	68.83	80.96
5APCr:FA/85BOS1/10C	27	44	20	1.92	2.41	70.04	93.82
5APCr:FA/60BOS1/Q/5C	36	38	13	2.07	2.50	81.91	65.71
5APCr:FA/55BOS1/Q/10C	33	42	15	2.02	2.51	80.75	64.72
95BOS1/5C	6	62	26	3.05	2.34	77.80	nd
17APCr/66BOS1/17CKD	35	60	3	2.40	2.39	91.60	nd
15APCr/61BOS1/15CKD/9C	61	11	1	4.03	2.34	72.08	80.28
11APCr/43BOS1/11CKD/Q/5C	67	20	3	3.06	2.42	79.79	49.08
10APCr/40BOS1/10CKD/Q/10C	45	32	7	2.03	2.46	92.31	nd
95BOS2/5C	4	70	18	1.44	2.31	78.7	nd
17APCr/66BOS2/17CKD	47	26	0	2.06	2.19	97.86	nd
16APCr/63BOS2/16CKD/5C	40	46	0	3.32	nd	87.13	nd
15APCr/60BOS2/15CKD/10C	4	66	0	2.99	2.27	80.97	nd
95BOS3/5C	7	33	31	0.52	nd	52.27	nd
14APCr/57BOS3/14CKD/15C	33	53	8	4.42	2.41	63.22	nd
11APCr/43BOS3/11CKD/Q/5C	36	37	12	3.70	2.47	81.14	nd
10APCr/40BOS3/10CKD/Q/10C	50	32	7	2.62	2.50	79.90	nd
16APCr/63BOS4/16CKD/5C	45	40	3	3.91	2.38	78.64	nd
15APCr/60BOS4/15CKD/10C	59	28	1	3.27	2.42	75.03	nd
10APCr/40BOS4/10CKD/Q/10C	31	39	13	2.04	2.51	86.75	nd
95BOS5/5C	3	77	17	3.33	nd	80.90	nd

The results indicated that the granules formed were primarily 4-10 mm in size. The resulting compressive strength (7 days) values of the granules significantly varied. For instance, the weakest granules (0.50 MPa) were obtained from 95BOS3/5C, whereas the strongest one (4.42 MPa) was achieved from 14APCr/57BOS3/14CKD/15C (Table 10). The compressive strength values were calculated for the 4-10 mm granule-size range, varying from 0.5 MPa (95BOS3/5C) to 4.4 MPa (14APCr/57BOS3/14CKD/15C) (Table 10). The main reason behind the lowest compressive strength of 95BOS3/5C could be the BOS3 sample's very slow hardening dynamics (Uibu et al., 2016). Generally, the mixtures that included MSWI APC residues, OS ashes and CKD resulted in stronger granules, compared to sole BOS1-5-based granules (i.e. 95BOS1/5C, 95BOS2/5C etc.). The incorporation of MSWI ashes 5%–100% and cement 5%–10% improved the compressive strength of the granules. This behaviour could be clarified by considering the presence of CaO, which may act as a potential binder by forming solid bridges in the granules. In parallel with this, the partial replacement (30%) of the cementitious wastes with inert and coarse quarry fines decreased the compressive strength values due to the lack of CaO reactive phases. In this study, the addition of cement led to inconsistent results. For instance, incorporating 9% cement resulted in a 68% increase in compressive strength in the case of 17APCr/66BOS1/17CKD, whereas adding 5% cement resulted in a 29% decrease in compressive strength in the case of 11APCr/43BOS3/11CKD/Q/5C. The factors adversely affecting compressive strength were discussed in **Paper III.** The current results suggest that the effect of processing conditions, especially the curing conditions, should be investigated in addition to the mixture compositions.

The compressive strength of the granules obtained after the leaching test was found to be higher (see **Paper II-Figure 8**). Strength development was improved by the exposure to water. The reason behind this fact could be that the delayed reactions may have been ceased owing to a lack of reactive water inside the granules (Uibu et al., 2016).

The granules' apparent densities varied between 1.75 g cm^{-3} (100APCr) and 2.51 g cm^{-3} (1APCr:FA/64OSA/Q/5C), indicating that the incorporation of higher APC residues led to lower densities (Table 10). Moreover, the leaching test did not result in a substantial change in the apparent density values (see **Paper II-Figure 9**).

3.1.4. Compositional changes and microstructure of ACT granulated waste

The changes in mineral composition of ACT granulated wastes were investigated by focusing on two sample granule batches (15APCr/61OSA/15CKD/9C and 5APCr:FA/85OSA/10C) (see **Paper III-Figure 2**). As the primary result of the ACT granulation process, the content of such carbonates as calcite and vaterite increased owing to the carbonation of free lime and other carbonatable compounds. The carbonates' phases were about 50%, while the contents of lime and portlandite in the both batches was negligible. The phases of quartz, belite, merwinite, akermanite, and K-feldspar were also dominant in both batches of granules. The source of chlorides such as NaCl, KCl and CaCl(OH) present in MSWI ashes and CKD played an important role in a significant amount of those in both batches. The content of ettringite was revealed as a new formation, and one of the strength-giving phases.

The FTIR analysis was employed to strengthen the results of the XRD analysis in terms of detecting carbonates and carbonatable contents, while observing the compositional changes in different layers of the granules (see **Paper III-Figure 4**). The results of the FTIR analysis indicated that: (1) the content of CO_3^{-2} ions significantly increased as a result of carbonation of the initial materials; (2) the observation of higher content of OH$^-$ ions in 95APCr/5C compared to the others supported the result of the low CO_2 binding degree of 95APCr/5C (49.87%) in comparison with BOS-based granules (Table 10), since it could represent the unreacted portlandite, CaCl(OH) and gypsum (Farmer, 1974; Siedl et al., 1969); (3) the stronger Si–O bands correlated with the addition of cement; (4) the presence of ettringite could be responsible for reaching a relatively high early strength in 95APCr/5C (3.93 MPa) (Duan et al., 2013; Uibu et al., 2016), in addition to the positive influence of C–S–H; and (5) the comparison of the different layers of the granules associated with the content of OH-, C=O and Si–O bonds supported the idea that the homogenous bond structure all around the granules could be one of the decisive factors for obtaining higher strength values (see **Paper III**).

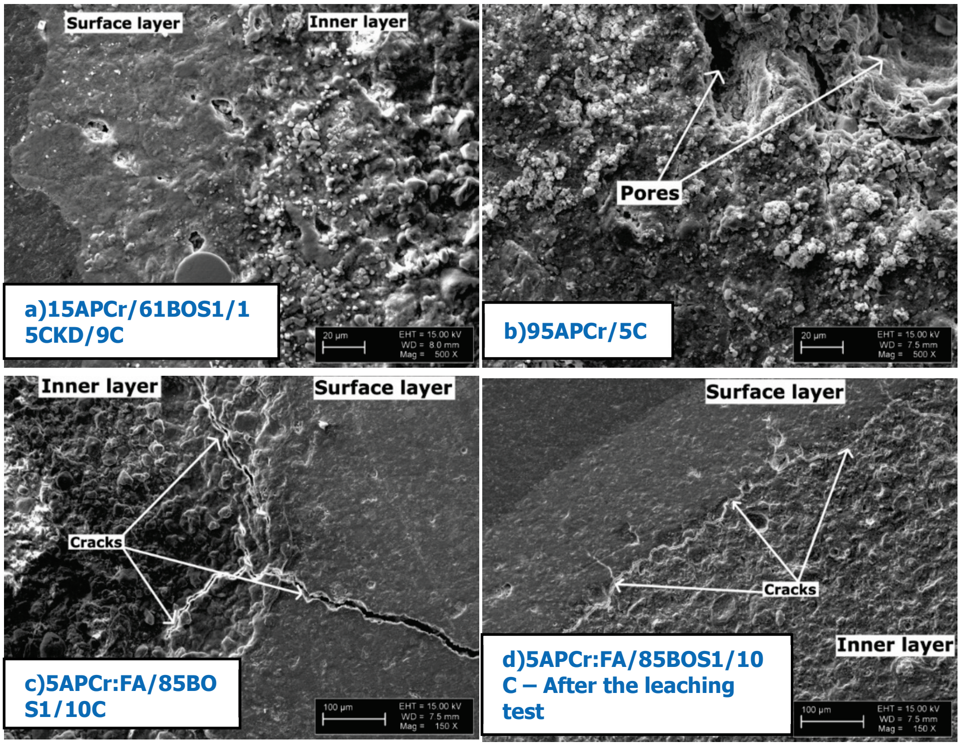

*Figure 9. SEM graphs of the ACT granulated waste (see **Paper III**)*

The scanning electron microscopy (SEM) photos revealed that the microstructure of the granules can have a remarkable effect on compressive strength values (Figure 9). For example, one of the strongest granule batches (15APCr/61OSA/15CKD/9C) was characterised by dense, uniform, and stabilised matrices (Figure 9(a)) without any cracks. In the case of 95APCr/5C, there were no boundary layers between the surface and the core (Figure 9(b)). The uniform structure could be one of the reasons for a relatively high compressive strength. The mixture of 5APCr:FA/85BOS1/10C experienced one of the lowest compressive strength values (Table 10). The SEM photos showed these granules to have many micro-cracks (Figure 9(c)). The SEM photo that was provided after the 24h leaching test (Figure 9(d)) indicated that the magnitude of the cracks was significantly decreased or had disappeared entirely, and the compressive strength of the leached granules (5APCr:FA/85OSA/10C) had increased to 4.74 MPa.

The MIP analysis indicated that the lowest total intruded volume and smallest mean pore size for the strongest granules (15APCr/61OSA/15CKD/9C) among measured samples (see **Paper III-Figure 6**). Decreasing the proportion of MSWI ashes in the mixtures from 95% to 1% caused an increase in the total intruded volume as well as in mean pore size. This indicates that larger pores can lead to cracks and voids. The incorporation of quarry fines (30%) had an adverse effect on the total intruded volume, while increasing the average pore size. The latter indicates that the inclusion of quarry fines most likely increased the apparent density of the granules, but not the compressive strength values.

3.1.5. Leaching characteristics of ACT granulated wastes

The leaching tests (Paper II, Paper III) were conducted on the size fraction of 4–10 mm granules. The tests indicated the following: (1) the leachable sulphate content of the granules was considerably below the hazardous limit of 50,000 mg/kg (Table 13, and **Paper II-Figure 6**); (2) the granules that were produced only from the OS ashes (i.e. 95BOS1/5C, 95BOS2/5C etc.) included leachable chloride content considerably lower than the limit of 25,000 mg/kg, whereas the mixtures that contained >15% MSWI ashes included chloride content significantly higher than the limit (see Table 13, **Paper III-Figure 8**, and **Paper II-Figure 6**); (3) since the heavy metal content and mobility of the OS ashes were not the concern, heavy metals such as Hg, Cd, Cr, Ni, Zn, Cu, As, Mo and Ba remained below the hazardous limit in all of the leachates for the OSA-based granules (see **Paper II-Table 3**); (4) only the leachate Pb content for the mixtures including MSWI APC residues and CKD exceeded the limit value set for hazardous waste (Table 11); (5) the OSA-based granules (i.e. 95BOS1/5C, 95BOS2/5C, 95BOS3/5C and 95BOS5/5C) achieved a leachate pH ≤ 11.5 (see **Paper II-Figure 7**); (6) some of the mixture-based granules (i.e. 17APCr/66BOS1/17CKD, 15APCr/60BOS2/15CKD/10C, 16APCr/63BOS4/16CKD/5C) were characterised by a pH ≤ 11.5 (see **Paper II-Figure 7**); however, generally the granules that contained >11% of MSWI ash had pH values higher than the limit (11.5) (**see** Table 11, and **Paper II, Figure 7**); (7) the leachates for BOS3-based mixtures remained deeply alkaline, which was also supported by the previous study (Uibu et al., 2016); (8) the EC levels of all the granules produced were below the hazardous limit (**see** Table 11, **Paper II-Figure 7**, and **Paper III-Figure 8**); (9) the addition of cement improved the water durability as well as the further immobilisation of chloride, sulphate, zinc and EC of the granules; (10) the leaching test did not result in a substantial change in the apparent density values (see **Paper II-Figure 8**); (11) mass loss during the leaching test led to a reduction in the size of the granules, and the outer surface changed into a smoother surface (see **Paper II-Figure 9**).

Table 11. The release of components from ACT granulated materials ('b' refers to the limit for landfilling of inert wastes, and 'c' to the landfilling limit for hazardous wastes) (Estonian Ministry of Environment, 2004).

Parameter	Limit (b)	Limit (c)	Unit	15APCr/60BOS2/15CKD/10C	11APCr/43BOS1/11CKD/Q/5C	11APCr/43BOS3/11CKD/Q/5C	15APC/61BOS1/15CKD/9C
pH	6-9		-	**11.8**	**11.6**	**12.6**	**11.7**
EC			mS/cm	13.10	10.10	13.70	12.4
TDS	4	100	g/kg	**65.5**	**50.5**	**68.5**	**68.5**
Chloride	0.8	25	g/kg	**31.3**	**24.4**	**24.7**	**30**
Fluoride	0.01	0.5	g/kg	<0.01	<0.01	<0.01	<0.01
Sulphate	1	50	g/kg	**14.2**	**8.25**	**8.76**	**8.9**
Ca			g/kg	9.8	6.5	10	7.5
K			g/kg	17.3	13.9	14	17.3
Na			g/kg	4.1	3.2	3.2	4.2
Mg			mg/kg	1.6	1.2	1	1.3
Mn			mg/kg	<0.1	<0.1	<0.1	<0.1
Hg	0.01	2	mg/kg	<0.002	<0.002	<0.002	<0.002
Cd	0.04	5	mg/kg	0.0093	<0.003	<0.003	<0.003
Pb	0.5	50	mg/kg	**65**	**28**	**1200**	**36**
Cr	0.5	70	mg/kg	**2**	**2.4**	**0.9**	**3**
Ni	0.4	40	mg/kg	<0.01	<0.01	<0.01	<0.01
Zn	4	200	mg/kg	<0.1	<0.1	0.1	<0.1
Cu	2	100	mg/kg	0.01	<0.01	0.02	0.05
As	0.5	25	mg/kg	0.007	<0.006	0.007	0.006
Mo	0.5	30	mg/kg	**1.2**	**1.9**	**1.3**	**2.1**
Ba	20	300	mg/kg	3.4	2.5	4.5	3.4

Considering that the incorporation of CKD and APC residues noticeably complicated the leaching behaviour of the granules produced, the further optimisation of the mixture composition would lead to their sustainable use. In order to produce environmentally safe construction materials, the hazardous MSWI wastes should be combined with environmentally benign or less hazardous industrial by-products, such as quarry fines and the OS ashes.

3.1.6. Potential end use for ACT-granulated products

Artificial aggregate produced from waste materials has major potential to be used as a secondary raw material in various engineering applications. The properties of artificial aggregate that are subject to its source material and the technology employed determine its potential end use. The main applications for artificial aggregate are geotechnical fill (Maghool et al., 2019), insulation applications (Zhang and Poon, 2015), masonry block production (Gunning et al., 2009), and structural concrete production (Lynn et al., 2016; Saha and Sarker, 2017; Zhou and Brooks, 2019).

In this study, the potential end use for ACT-granulated products could be masonry block production and structural concrete production, due to the mechanical and technological results obtained. A similar example could be seen from Carbon8, a spin-off company of the University of Greenwich, in England, which utilises waste residues to manufacture carbon-neutral masonry blocks and sustainable concrete.

3.2. Economic aspects

In this chapter, the economic aspects of the chosen scenarios are discussed by employing CBA. The main objective of this analysis was to assess whether the proposed technological solutions (DRH carbonation and ACT granulation) for utilising waste ashes and CO_2 in Estonia would be economically feasible. In the analysis, DRH carbonation was considered to treat only MSWI ash from Iru Power Plant. However, in the ACT granulation technology scenarios, two different batches (5APCr:FA/90BOS1/5C and 15APCr/61BOS1/15CKD/9C) were chosen as references based on the results of Section 3.1. The main reason for this was that these mixtures were found to possess relatively better engineering and environmental properties than the other mixtures.

3.2.1. Description of scenarios with costs and benefits

The economic aspects of three different scenarios was analysed. The scenarios, along with the options and descriptions, are given in Table 12.

Table 12. Description of scenarios and options

Scenario	Description
DRH-Carbonation Case	
Base case	MSWI ash is delivered to a neighbouring company
Option 1	A DRH carbonation plant is constructed at Iru Power Plant to treat MSWI ash. The treated residue is utilised in any other sector originated from the waste-to-product principle
Option 2	A DRH carbonation plant is constructed at Iru Power Plant to treat MSWI ash. The treated residue is sent to a landfill site near Tallinn
ACT Granulation Case 1	
Base Case	Eesti Energia AS does not invest in ACT granulation technology and continues to landfill oil shale ashes and to deliver MSWI ashes to a hazardous-waste management company
Option 1	An ACT granulation plant is constructed next to Auvere power plant. The plant produces aggregates from MSWI ashes, oil shale ashes and ordinary Portland cement. The mixture of 5APCr:FA/90BOS1/5C was taken as a reference. The products are entered into an aggregate market

Option 2	The difference between Option 1 and Option 2 is that the mixture of 15APCr/61BOS1/15CKD/9C was taken as a reference
ACT Granulation Case 2	
Base case	AS Kunda Nordic Tsement does not invest in ACT-granulation technology
Option 1	An ACT granulation plant is constructed next to Kunda Nordic Tsement plant. The plant produces aggregates from MSWI ashes, oil shale ashes and ordinary Portland cement. The mixture of 5APCr:FA/90BOS1/5C was taken as a reference. The products are entered into an aggregate market
Option 2	The difference between Option 1 and Option 2 is that the mixture of 15APCr/61BOS1/15CKD/9C was taken as a reference

In the CBA analysis, it is recommended that costs and benefits are monetised for each scenario. Table 13 presents the categories of monetised costs and benefits for each scenario.

Table 13. Monetised costs and benefits for each scenario

Costs for Option 1 and Option 2	Benefits from Option 1 and Option 2
DRH-Carbonation Case	
CAPEX	Reduction in treatment cost
OPEX	Reduction in transportation cost
ACT-Granulation Case 1	
CAPEX	Reduction in treatment and transportation costs of MSWI ashes
OPEX	Reduction in amount of environmental charges paid for oil shale ash disposal
	Reduction in CO_2 emissions allowance payment
	Sale of aggregate
ACT-Granulation Case 2	
CAPEX	Sale of aggregate
OPEX	Reduction in CO_2 emissions allowance payment
	Revenue for handling MSWI ashes

3.2.2. Monetisation of costs and benefits with NPV, IRR and BCR

DRH-carbonation case

The base case scenario of DRH-carbonation contains only one monetised cost composed of the treatment and transportation costs of FA. As a result, no monetised benefit is gained. The scenario involves no changes in the current situation. The annual APC residues and FA generation at Iru Power Plant amount to 10,900t (Enefit Renewable Energy, 2017). The treatment and transportation cost for the ashes is 2,000,000 EUR annually, based on market research. For the base case scenario of DRH-carbonation, the NPV was found to be −16,870,663 EUR at the end of 2025 under the base case scenario. However, it is unreasonable to calculate either the IRR or the BCR because there is no monetised benefit in the base case scenario (see **Paper I, Figure 3(a)** for the discounted cash flows for the period between 2016 and 2025).

For both Option 1 and Option 2 of DRH-carbonation, an investment should firstly be made to construct the desired carbonation plant. The capacity of the plant is set at 11,000t per year. The CAPEX was determined approximately at 4,000,000 EUR. This consists of major equipment, land use, construction and installation labour costs, transportation and civil infrastructure. The investment includes 1,500,000 EUR for major equipment, such as a mixing tank, stabilisation tank, vacuum belt filter, scrubber and flue gas compressor, and excludes pipelines and pumps. The other part of the CAPEX is approximately 2,500,000 EUR, which covers land use, labour, transportation and construction costs.

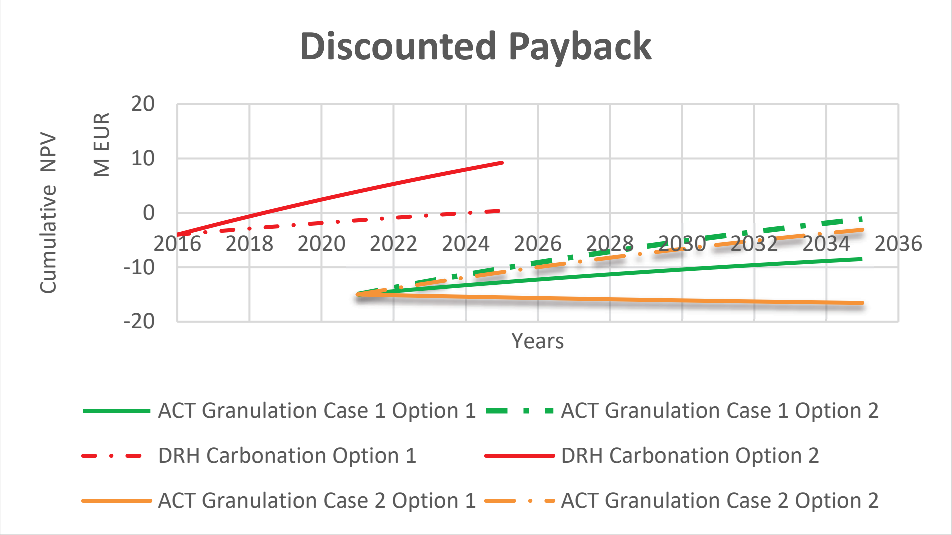

Figure 10. Discounted payback period for the options of DRH carbonation, ACT Granulation Case 1 and ACT Granulation Case 2. NPV: Net Present Value.

The annual maintenance cost for a DRH carbonation plant is determined as 2% of the investment cost. This figure includes the replacement of worn parts, such as pH-probes, CO_2 injection nozzles and spare parts. Additionally, specialists who service special parts will incur an external cost. Altogether, maintenance costs will amount to 80,000 EUR per year. The annual operation cost is 107,393 EUR (see **Paper I-Table 2**). The other cost component is labour cost. The plant operation requires three full time employees.

This number may change depending on the ongoing requirements and circumstances. The relevant cost was calculated at 36,000 EUR per year.

The annual OPEX cost of DRH carbonation Option 1 is 223,393 EUR. At the end of 2025, under Option 1, the NPV, IRR and BCR will be 9,209,662 EUR, 43% and 2.63, respectively. This amount fundamentally represents the NPV of the profit from the loss end of the 10 years compared to the base case scenario (see **paper I-Figure 3(b)** for the discounted cash flows). The cumulative NPV values for DRH carbonation Option 1 and Option 2 are given in Figure 10.

Under DRH carbonation Option 2, the treated FA will be delivered to Tallinn's landfill site, which is 10.8 km away from Iru Power Plant. The cost of transportation by trucks per t of FA per km is 0.07 EUR. This comprises an annual transportation cost of 11,330 EUR at 14,987 t of annual carbonated FA. The landfilling fee for stabilised waste is 78.41 EUR per t at Estonian landfills. The annual disposal cost for carbonated APC residue and FA is 1,175,131 EUR. Therefore, the annual OPEX cost of DRH carbonation Option 2 is 1,409,854 EUR. At the end of 2025, under Option 2, the NPV, IRR and BCR will be 387,931 EUR, 6% and 1.03, respectively. This indicates that Option 2 has better economical results than the base case scenario (see **Paper I-Figure 3(c)** for the discounted cash flows).

ACT Granulation case

For all the options under both ACT granulation Case 1 and ACT granulation Case 2, an investment should first be made to construct the desired carbonation plant. The capacity of the plant was anticipated to be 70,000 t per year. The CAPEX was determined at 15,000,000 EUR. This data is modified in light of the assumption that the Carbon8 company employs ACT granulation technology to produce aggregates from several industrial waste materials (Carbon8, 2018).

The maintenance cost for the ACT granulation plant is determined as 2% of the investment cost. The maintenance cost amounts to 300,000 EUR per year. The operational cost of the plant is assumed to be 150,000 EUR. The other cost component is job-creation. It was decided to hire 10 employees during the operation. This number may change depending on the ongoing requirements and circumstances. The relevant cost was calculated at 204,000 EUR per year.

The base case scenario of ACT granulation Case 1 is that Eesti Energia AS does not invest in ACT granulation technology and continues to landfill oil shale ashes and to deliver MSWI ashes to a hazardous-waste management company.

To operate at the capacity of 70,000t per year under ACT granulation Case 1 Option 1, the plant would require 63,000t of oil shale ashes, 3,500 t of MSWI ashes and 3,500 t of OPC according to the reference mixture 5APCr:FA/90BOS1/5C. The cost of OPC for a wholesale was decided as 2.5 EUR per 20 kg based on a market research. Therefore, the cost of raw materials for ACT granulation Case 1 Option 1 is 437,500 EUR.

Under ACT granulation Case 1 Option 1, MSWI ashes from Iru Power Plant are transported to Auvere power plant (200 km). The cost of transportation by trucks per t of FA per km is 0.07 EUR. This comprises an annual transportation cost of 49,000 EUR. Overall, the annual OPEX of ACT granulation Case 1 Option 1 including maintenance, operation and labour cost, is 1,140,500 EUR.

The monetisation of benefits of ACT-granulation Case 1 Option 1 are the following: (1) the approximate amount of aggregates produced from the mixture of 5APCr:FA/90BOS1/5C with an annual operational capacity of 70,000 t is 96,667 t, owing to CO_2 captured and water used. Considering that the average market price of aggregates is around 8 EUR (Carbon8, 2018), the annual revenue from the sale of aggregate is anticipated at 773,336 EUR; (2) CO_2 will be sequestrated from the flue gas of Auvere power plant. The amount of CO_2 bound for 5APCr:FA/90BOS1/5C is 80.96 kg per ton of waste (Table 10), and therefore 5,667 t for 70,000 t of waste materials. The reduction in CO_2 emissions allowance cost for Auvere power plant is calculated at 152,442 EUR; (3) since 63,000 t of OSA will no longer be sent to landfill, the reduction in tax paid for OSA disposal would be 189,000 EUR, since the landfilling tax per t of OSA is 3 EUR; (4) since 3,500 t of MSWI ashes will no longer be delivered to a hazardous-waste management company, the reduction in treatment and transportation cost for MSWI ashes would be 642,201 EUR. Overall, the total monetised benefit under ACT granulation Case 1 Option 1 is 1,756,980 EUR. At the end of 2035, under ACT-granulation Case 1 Option 1, the NPV, IRR and BCR will be -8,488,046 EUR, -7% and 0.69, respectively. The cumulative NPV values for ACT-granulation Option 1 and Option 2 are given in Figure 10.

Under ACT granulation Case 1 Option 2, the plant would require 42,700 t of oil shale ashes, 10,500 t of MSWI ashes, 10,500 t of CKD and 6,300 t of OPC annually, according to the reference mixture 15APCr/61BOS1/15CKD/9C. The cost of OPC for a wholesale was decided as 2.5 EUR per 20 kg based on market research. Therefore, the cost of raw materials for ACT granulation Case 1 Option 1 is 787,500 EUR. The MSWI ashes from Iru Power Plant, and CKD from Kunda cement factory are transported to Auvere power plant (200 km and 104 km, respectively). This comprises an annual transportation cost of 223,440 EUR. Overall, the annual OPEX of ACT granulation Case 1 Option 1, including maintenance, operation and job-creation, is 1,664,940 EUR.

The monetisation benefits of ACT granulation Case 1 Option 2 are the following: (1) the approximate amount of aggregates produced from the mixture of 15APCr/61BOS1/15CKD/9C with an annual operational capacity of 70,000t is 96,620t owing to CO_2 captured and water used. The annual revenue from the sale of aggregate is anticipated at 772,960 EUR; (2) CO_2 will be sequestrated from the flue gas of Auvere power plant. The amount of CO_2 bound for 15APCr/61BOS1/15CKD/9C is 80.28kg per t of waste (Table 12), and therefore 5,620t for 70,000t of waste materials. The reduction in CO_2 emissions allowance cost for Auvere plant is calculated at 151,178 EUR; (3) since 42,700t of OSA will no longer be sent to landfill, the reduction in tax paid for OSA disposal would be 128,100 EUR, since the landfilling tax for per t of OSA is 3 EUR; (4) since 10,500t of MSWI ashes will no longer be delivered to a hazardous-waste management company, the reduction in treatment and transportation cost for the MSWI ashes would be 1,926,605 EUR. Overall, the total monetised benefit under ACT granulation Case 1 Option 1 is 2,978,843 EUR. At the end of 2035, under ACT granulation Case 1 Option 2, the NPV and BCR will be -1,121,081 EUR, and 0.97, respectively.

The base case scenario of ACT granulation Case 2 is that AS Kunda Nordic Tsement does not invest in ACT-granulation technology. Therefore, no calculations were made for the base case scenario.

To operate at the capacity of 70,000t per year, the plant would require 63,000 t of oil shale ashes, 3,500 t of MSWI ashes and 3,500 t of OPC, according to the reference mixture 5APCr:FA/90BOS1/5C under ACT granulation Case 2 Option 1. The cost spent on buying oil shale ashes (i.e. BOS1) is 315,000 EUR, since the market price for oil shale ashes is approximately 5 EUR per t. The wholesale cost of OPC was set at 2.5 eur per 20kg based on market research. However, this price is kept below the market price of OPC since Kunda Nordic Tsemet AS produces its own OPC. Therefore, the cost of raw materials for

ACT-granulation Case 2 Option 1 is 577,500 EUR. Under ACT-granulation Case 2 Option 1, MSWI ashes from Iru Power Plant, and oil shale ashes from Auvere power plant are transported to Kunda cement plant (100 km and 104 km, respectively). The cost of transportation by trucks per t of FA per km is 0.07 EUR. This comprises an annual transportation cost of 483,140 EUR. Overall, the annual OPEX of ACT granulation Case 2 Option 1 is 1,714,640 EUR.

The monetisation benefits of ACT granulation Case 2 Option 1 are the following: (1) the approximate amount of aggregates produced from the mixture of 5APCr:FA/90BOS1/5C with an annual operational capacity of 70,000t is 96,667t, owing to CO_2 captured and water used. Considering that the average market price of aggregates is around 8 EUR (Carbon8, 2018), the annual revenue from the sale of aggregate is anticipated as 773,336 EUR; (2) CO_2 will be sequestrated from the flue gas of Kunda cement plant. The amount of CO_2 bound for 5APCr:FA/90BOS1/5C is 80.96 kg per t of waste (Table 10), and therefore 5,667 t for 70,000 t waste materials. The reduction in CO_2 emissions allowance cost for the Kunda plant is calculated at 152,442 EUR; (3) since the treatment and transportation cost for the MSWI ashes is 2,000,000 EUR annually based on market research as discussed in the DRH Carbonation Case, the revenue for utilising 3,000t of MSWI ashes in ACT granulation Case 2 Option 1 is 642,201 EUR. Overall, the total monetised benefit under ACT-granulation Case 2 Option 1 is 1,567,980 EUR. At the end of 2035, under ACT-granulation Case 2 Option 1, the NPV, IRR and BCR will be -16,549,188 EUR, 0% and 0.50, respectively.

Under ACT granulation Case 2 Option 2, the plant would require 42,700t of oil shale ashes, 10,500t of MSWI ashes, 10,500t of CKD and 6,300 t of OPC annually according to the reference mixture 15APCr/61BOS1/15CKD/9C. The cost of buying oil shale ashes (i.e. BOS1) is 213,500 EUR, since the market price for oil shale ashes is approximately 5 EUR per t. The cost of OPC was set at 2.5 EUR per 20kg. However, this price is kept below the market price of OPC since AS Kunda Nordic Tsemet produces its own OPC. Therefore, the cost of raw materials for ACT-granulation Option 2 is 686,000 EUR. Under ACT-granulation Case 2 Option 2, MSWI ashes from Iru Power Plant, and oil shale ashes from Auvere power plant are transported to Kunda cement plant (100 km and 104 km, respectively). The cost of transportation by trucks per t of FA per km is 0.07 EUR. This comprises an annual transportation cost of 384,356 EUR. Overall, the annual OPEX of ACT granulation Case 2 Option 2 is 1,724,356 EUR.

The monetisation benefits of ACT granulation Case 2 Option 2 are the following: (1) the approximate amount of aggregates produced from the mixture of 15APCr/61BOS1/15CKD/9C with an annual operational capacity of 70,000t is 96,620t, owing to CO_2 captured and water used. Considering that the average market price of aggregates is around 8 EUR (Carbon8, 2018), the annual revenue from the sale of aggregate is anticipated at 772,960 EUR; (2) CO_2 will be sequestrated from the flue gas of Kunda cement plant. The amount of CO_2 bound for 15APCr/61BOS1/15CKD/9C is 80.28 kg per t of waste (Table 10), and therefore 5,620 t for 70,000 t of waste materials. The reduction in CO_2 emissions allowance cost for the Kunda plant is calculated at 151,178 EUR; (3) since the treatment and transportation cost for the MSWI ashes is 2,000,000 EUR annually based on market research, as discussed in the DRH-carbonation case, the revenue for utilizing 10,500 t of MSWI ashes in ACT-granulation Option 2 is approximately 1,926,605 EUR. The total monetised benefit under ACT granulation Case 2 Option 2 is 2,850,743 EUR. At the end of 2035, under ACT granulation Case 2 Option 2, the NPV, IRR and BCR will be -3,101,836 EUR, 0% and 0.91, respectively.

3.2.3. Sensitivity analysis

In practice, substantial uncertainties are always likely to be found in calculations in the CBA analysis. The significance of monetised sources may change, which may affect the results both a positive and negative way.

Firstly, the change of the NPV was discussed depending on different discount rates. In this study, the optimum discount rate was determined at 0.04. The changes in NPV at discount rates of 0.03 and 0.07 were investigated. In addition, García-Gusano et al. (2016) recommend using a reference value not higher than 4–5% in European countries. Tables 14-15-16 present the NPV changes with different discount rates for costs, benefits and the total under DRH carbonation, ACT Granulation Case 1-2, and the base case scenarios.

Table 14. Discount rates of 3% and 7% compared to 4% base and assumptions altered for the cost source for DRH carbonation options and the base case.

<table>
<tr><th colspan="4">DRH Carbonation Case</th></tr>
<tr><td colspan="4">Option 1</td></tr>
<tr><td>Assumptions</td><td>NPV - Costs [€]</td><td>NPV -Benefits [€]</td><td>NPV - Total [€]</td></tr>
<tr><td>P_x = 3%</td><td>5,739,370</td><td>15,572,218</td><td>9,832,848</td></tr>
<tr><td>P_x = 4%</td><td>5,661,008</td><td>14,870,663</td><td>9,209,662</td></tr>
<tr><td>P_x = 7%</td><td>5,455,457</td><td>13,030,464</td><td>7,575,001</td></tr>
<tr><td>20% Cost Decrease (P_x= 4%)</td><td>5,993,201</td><td>14,870,663</td><td>8,877,462</td></tr>
<tr><td>20% Cost Decrease (P_x= 4%)</td><td>5,328,801</td><td>14,870,663</td><td>9,541,862</td></tr>
<tr><td colspan="4">Option 2</td></tr>
<tr><td>Assumptions</td><td>NPV - Costs [€]</td><td>NPV - Benefits [€]</td><td>NPV - Total [€]</td></tr>
<tr><td>P_x = 3%</td><td>14,977,277</td><td>15,572,218</td><td>594,941</td></tr>
<tr><td>P_x = 4%</td><td>14,482,732</td><td>14,870,663</td><td>387,931</td></tr>
<tr><td>P_x = 7%</td><td>13,185,526</td><td>13,030,464</td><td>-155,062</td></tr>
<tr><td>20% Cost Decrease (P_x= 4%)</td><td>16,579,278</td><td>14,870,663</td><td>-1,708,615</td></tr>
<tr><td>20% Cost Decrease (P_x= 4%)</td><td>12,386,186</td><td>14,870,663</td><td>2,484,478</td></tr>
<tr><td colspan="4">Base Case</td></tr>
<tr><td>Assumptions</td><td>NPV - Costs [€]</td><td>NPV - Benefits [€]</td><td>NPV - Total [€]</td></tr>
<tr><td>P_x = 3%</td><td>17,572,217</td><td>0</td><td>-17,572,217</td></tr>
<tr><td>P_x = 4%</td><td>16,870,663</td><td>0</td><td>-16,870,663</td></tr>
<tr><td>P_x = 7%</td><td>15,030,464</td><td>0</td><td>-15,030,464</td></tr>
</table>

Table 14 shows that the total NPV with a 7% discount rate under DRH Carbonation Option 1 still presented a fairly substantial profit. It shows that the NPV would not move below zero in a worst-case scenario. However, the total NPV with a discount rate of 7% under DRH Carbonation Option 2 was nevertheless negative. This indicates that it cannot be above zero in a worst-case scenario. For the options of ACT Granulation Case 1 and

Case 2, the total NPV values with 3% and 7% discount rates were well below zero, which indicates that the deviation of the discount rate between 3-7% will not result in a positive value of the total NPV values in both cases (Table 15 and Table 16).

Table 15. Discount rates of 3% and 7% compared to 4% base and assumptions altered for the cost source for ACT Granulation Case 1 options and the base case

ACT Granulation Case 1			
Option 1			
Assumptions	NPV - Costs [€]	NPV -Benefits [€]	NPV - Total [€]
P_x = 3%	27,883,171	19,846,975	-8,036,197
P_x = 4%	27,047,242	18,559,196	-8,488,046
P_x = 7%	24,974,206	15,365,612	-9,608,594
20% Cost Increase (P_x= 4%)	29,456,690	18,559,196	-10,897,494
20% Cost Decrease (P_x= 4%)	24,637,793	18,559,196	-6,078,598
Option 2			
Assumptions	NPV - Costs [€]	NPV - Benefits [€]	NPV - Total [€]
P_x = 3%	33,807,284	33,649,228	-158,056
P_x = 4%	32,586,966	31,465,885	-1,121,081
P_x = 7%	29,560,679	26,051,376	-3,509,303
20% Cost Increase (P_x= 4%)	36,104,359	31,465,885	-4,638,474
20% Cost Decrease (P_x= 4%)	29,069,573	31,465,885	2,396,312
Base Case			
Assumptions	NPV - Costs [€]	NPV - Benefits [€]	NPV - Total [€]
P_x = 3%	-	-	-
P_x = 4%	-	-	-
P_x = 7%	-	-	-

Secondly, it is important to analyse the change in the sources of costs to see the variations of the total NPV after the project lifetime (10 years for DRH Carbonation and 15 years for ACT Granulation Case 1-2). For instance, OPEX including maintenance cost, raw material cost, transportation cost, job creation cost etc. may vary in the future. Therefore, the cost sources are increased and decreased by 20%. Moreover, the way in which total NPV responds to this change is analysed for the different options. Also, the decrease in cost sources will result in a higher NPV, as desired. Table 16 shows that since the cost is not high in the DRH Carbonation Case, the change in the total NPV is lowest under Option 1. As a result, Option 2 has higher costs, and the response to this change was rather significant. It was observed that Option 2 had a negative value for a 20% increase in the cost sources. In this case, Option 2 would not be a better economical option than the base case scenario. An attempt has been made to analyse alternatives for the changes that are likely to occur over 10 years. The results showed that the total

NPVs of the carbonation waste-to-product scenario even showed positive results in a worst-case scenario. Moreover, the change in NPV over the years with different discount rates is not vital.

Table 16. Discount rates of 3% and 7% compared to 4% base and assumptions altered for the cost source for ACT Granulation Case 2 options and the base case

ACT Granulation Case 2			
Option 1			
Assumptions	NPV - Costs [€]	NPV -Benefits [€]	NPV - Total [€]
P_x = 3%	34,368,699	17,712,017	-16 656 682
P_x = 4%	33,111,953	16,562,765	-16,549,188
P_x = 7%	29,995,329	13,712,719	-16,282,610
20% Cost Increase (P_x= 4%)	36,734,344	16,562,765	-20,171,578
20% Cost Decrease (P_x= 4%)	29,489,562	16,562,765	-12,926,797
Option 2			
Assumptions	NPV - Costs [€]	NPV - Benefits [€]	NPV - Total [€]
P_x = 3%	34,478,451	32,202,201	-2,276,250
P_x = 4%	33,214,584	30,112,749	-3,101,836
P_x = 7%	30,080,300	24,931,082	-5,149,219
20% Cost Increase (P_x= 4%)	36,857,501	30,112,749	-6,744,753
20% Cost Decrease (P_x= 4%)	29,571,668	30,112,749	541,081
Base Case			
Assumptions	NPV - Costs [€]	NPV - Benefits [€]	NPV - Total [€]
P_x = 3%	-	-	-
P_x = 4%	-	-	-
P_x = 7%	-	-	-

Under the options of ACT Granulation Case 1-2, a 20% increase in cost sources further decreased the negative total NPV values of the options. However, only the total NPV value of ACT Granulation 1 Option 2 and ACT granulation 2 Option 2 remained above zero with a 20% cost decrease. This shows that construction of an ACT granulation plant at Kunda cement plant or at Auvere power plant would not be economically profitable compared to the base case scenarios without any reduction in cost elements. The best-case scenario showed an ACT granulation plant could be profitable at Auvere plant, but only if the cost of components would decrease by 20%, giving the total NPV value at 2,396,312 EUR in the end of 15 years.

4. Conclusions

This dissertation elucidated the technological and economic feasibility of utilising different types of industrial wastes from municipal solid waste incineration, Estonian oil shale combustion, and cement production for carbonation-based stabilisation, as a solution for the huge amount of CO_2 emissions and enormous ash accumulations in Estonia. Accelerated carbonation technology with granulation (ACT granulation) was tested on different oil shale ashes, municipal solid waste incineration fly ashes, and cement kiln dust, while DRH accelerated carbonation technology without granulation was theoretically evaluated on the stabilisation of municipal solid waste incineration fly ashes.

The novel ACT granulation technology was found to have a remarkable potential, in mitigating both the release of CO_2 emissions, and the environmental impact of the industrial waste ashes associated with power and cement production in Estonia. The primary outcomes of the experimental part can be summarised as follows:

1. CO_2 uptake is mainly attributed to the free lime content in waste ashes, which is relatively high (8%–15%) in oil shale ashes and MSWI APC residue, but negligible in CKD, MSWI FA, OPC, and quarry fines
2. The reactivity of oil shale ashes with CO_2 was higher than that of MSWI APC residue under the conditions, which included a low-range water-to-solid ratio (~0.30 w/w) and a gas flow of 20% CO_2 in air, since MSWI APC residue shows an early stage agglomeration, which in turn inhibits CO_2 diffusion and the following carbonation reaction
3. The $\mathrm{BD}_{\mathrm{CO_2}}$ values of ACT granulated products were within the range of 50%–98%, indicating that the carbonation efficiency deviated from moderate to high, depending upon the mixture's composition
4. The amount of CO_2 that was bound into those granules that included the mixture of MSWI APC residues, OSA, CKD and 5%-9% OPC reached up to around 80 kg per t of waste. Adding quarry fines and CKD as carbonates containing fillers into the mixture proportionally decreased the amount of CO_2 bound per t of waste
5. The granules produced were characterised by a size range of 4–10 mm and possessing a regular shape. The granules that included the mixture of MSWI APC residues, OSA, CKD and 5%-9% OPC had a compressive strength of 4.03MPa. The incorporation of MSWI ashes 5%–100% and cement 5%–10% enhanced the compressive strength of the granules. The granules that contained mainly OSA remained noticeably weaker, and the partial replacement of the cementitious wastes with inert and coarse quarry fines decreased the compressive strength further
6. Adding OPC did not result in a proportional increase in compressive strength, but the inclusion of it enhanced water-durability and the further immobilisation of chloride, sulphate, and EC by more than 5%
7. The granules' apparent densities varied between 1.75 g cm^{-3} and 2.52 g cm^{-3}. Higher APC residues incorporation led to lower densities
8. The MIP and SEM analysis confirmed that compressive strength does not only depend upon the content of strength-giving phases (the added OPC), but also on the physical structure and microstructure. The dense and uniform structure

resulted in a higher compressive strength, as the weakest granules were characterised by visible intersections between layers, pores, and cracks

9. A substantial decline in the pH levels and electrical conductivity values of the leachate in the ACT granulated products was obtained. The granules that contained >11% of MSWI ash had pH values that were above the limit (11.5). These batches also suffered significant mass loss during the leaching test
10. The APC residue-based granules tended to decompose in water, and the leaching of chloride was well over the limit of 25 g kg^{-1}
11. The ACT granulation significantly reduced the mobility of zinc
12. In order to produce environmentally safe construction materials, the hazardous MSWI wastes should be combined with environmentally benign, or less hazardous, industrial by-products such as quarry fines and OSA

Moreover, the main outcomes of the economic analysis can be summarised as follows:

1. Both of the options proposed under the DRH carbonation scenario in which MSWI fly ashes are carbonated and utilised were better economic solutions compared to the base case scenario over a 10-year period
2. The carbonation of MSWI fly ashes in the waste-to-product concept had a better economic result compared to the landfilling scenario in DRH Carbonation scenarios
3. The construction and operation of an ACT granulation plant at Auvere Power Plant or Kunda Cement Plant in order to utilise waste ashes from MSWI, OS and cement sectors were found to be economically inefficient. After 15 years, NPV values would still be negative
4. The sensitivity analysis indicated that construction and operation of an ACT granulation plant at Auvere and Kunda plants would be profitable after 15 years in the event of a 20% cost decrease. A varying discount rate of 3-7% did not result in positive NPV results in either case

The results of this study provide a way of utilising waste from the MSWI, power, and cement sectors, closely associated with a circular economy concept in line with the targets.

Further research will extensively focus on the following: (1) further optimisation of mixtures to produce ACT-granulated products; (2) the mechanical and technological performance of ACT-granulated products in masonry block and structural concrete productions; (3) comprehensive market research for ACT-granulated products and/or masonry block and structural concrete produced from ACT-granulated products as a secondary raw material; (4) improved CBA analysis considering the utilisation of the majority of waste residues in Estonia with positive and normative approaches; (5) experimenting with DRH-Carbonation technology at laboratory scale; and (6) A comprehensive CBA should be conducted where the price fluctuations of the cost and benefit sources are taken into consideration.

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Abstract

Accelerated Carbonation Treatment of Industrial Wastes: Physicochemical, Environmental and Economic Aspects

Meeting the ever-increasing world energy demand in a sustainable way is one of the greatest challenges faced by humanity today. The use of fossil fuels currently accounts for more than 80% of global energy consumption, while it is anticipated to remain a primary energy source in 2040. The extensive use of fossil fuels in energy production has resulted in a historically high level of CO_2 emissions, and significant amounts of industrial by-products. Considering that social and industrial progress generally comes at an environmental price, it is of the utmost importance that the environmental burden that results from CO_2 emissions and hazardous industrial wastes is substantially mitigated for sustainable development.

In the Republic of Estonia, the primary energy source is a local, low-grade carbonaceous fossil fuel: Estonian oil shale. The Estonian oil shale industry is the largest CO_2 emitter, as well as being a source of large amounts of waste ash. Oil shale ashes which originate from pulverised firing and circulating fluidised bed combustion technologies are dominated by a large amount of free lime content, which is the main concern for disposal. Only 1%–3% of oil shale ash is currently utilised in construction materials or the agricultural industry, leaving about 7m tons to be deposited in ash fields every year. Solid residues produced by municipal solid waste incineration (MSWI) and the cement industry generate another significant waste stream in Estonia. MSWI fly ashes are classified as a hazardous waste, and there is currently no treatment technology applied in Estonia. The extensive amounts of CO_2 emissions and industrial solid residues are among the most serious environmental problems that Estonia currently faces.

The aim of this study was to provide a method for utilising CO_2 and waste from the oil shale, MSWI and cement sectors, focusing on chemical, technological and economic concepts. The use of accelerated carbonation technology, in combination with a granulation process, was employed to produce construction aggregates from CO_2 and the relevant solid wastes, in light of a waste-to-product concept. In addition, the accelerated carbonation of MSWI fly ashes was theoretically assessed. The economic aspects of the proposed scenarios were evaluated by conducting a Cost & Benefit Analysis.

The results showed that the waste ashes from the oil shale, MSWI, and cement sectors qualify as a suitable sorbent for CO_2 capture in ACT granulation process. The CO_2 binding ability of waste depended primarily upon the content of free lime and calcium-bearing silicates. The varying granule composition had a significant effect upon the basis of CO_2 uptake, strength development, leaching behaviour, microstructure, and morphology. Generally, mixtures of different wastes (i.e. incorporation of MSWI ashes) after the inclusion of cement led to stronger aggregates compared to oil shale ash-based granules. The results indicated that the compressive strength of the products does not only depend on the content of strength-giving phases, but also on the physical structure and microstructure. Moreover, leachable chloride compounds present in the granules had an adverse effect on the water durability of the granules. The process was found to be effective in diminishing the pH levels and electrical conductivity values of the leachate. Additionally, the ACT granulation process significantly reduced the mobility of zinc. All in all, in order to produce environmentally safe construction materials, hazardous

MSWI wastes should be combined with environmentally benign or less hazardous industrial by-products, such as oil shale ash.

The economic aspects of CO_2 utilisation in the stabilisation of waste ashes from the oil shale, MSWI, and cement sectors indicated that there could be a private return on investment in the case of employing only MSWI ashes in the utilisation process, whereas there may not be a private return on investment in the primary utilisation of the extensive amount of oil shale ash, since significant attention should be paid to the social returns (i.e. reducing environmental degradation, improving wellbeing, mitigating climate change, and other related social benefits).

Finally, the results of this study could assist in closing the cycle of waste in the energy and cement sectors, so as to reach national and international targets of promoting waste recovery, diminishing waste disposal, and mitigating climate change for a sustainable future.

Lühikokkuvõte

Tööstusjäätmete töötlemine kiirendatud karboniseerimismeetodil: füüsikalis-keemilised, keskkonnaalased ja majanduslikud aspektid

Üks suurimaid praegu inimkonna ees seisvaid väljakutseid on rahuldada maailma aina kasvav energiavajadus kestlikul moel. Fossiilkütuste kasutus moodustab rohkem kui 80% maailma energiatarbimisest ning eeldatakse, et see jääb peamiseks energiaallikaks ka aastal 2040. Fossiilkütuste ulatuslik kasutus energiatootmises on toonud kaasa ajaloo kõrgeima CO_2 kontsentratsiooni atmosfääris ja tööstusjäätmete lademed. Arvestades, et ühiskondliku ja tööstusliku arengu hinda maksab tavaliselt keskkond, on kestliku arengu jaoks äärmiselt tähtis CO_2 heidetest ja ohtlikest tööstusjäätmetest tekkivat keskkonnakoormust oluliselt vähendada.

Eesti Vabariigis on peamiseks energiaallikaks Eesti põlevkivi ehk kohalik madala kasuteguriga süsinikku sisaldav fossiilkütus. Eestis on põlevkivitööstus peamine CO_2 emissioonide allikas ja ka suurtes kogustes tuhajäätmete tekitaja. Põlevkivituhale on iseloomulik suhteliselt suur vaba lubja sisaldus, mis teeb tema keskkonda ladestamise problemaatiliseks, samas loob eeldused tema kasutamiseks ehitusmaterjalitööstuses või põllumajanduses. Praegu läheb taaskasutusse ainult 1%–3% põlevkivituhast, mis jätab igal aastal umbes 7 miljonit tonni tuhka tuhaväljadele. Munitsipaaljäätmete põletamisest (MJP) ja tsemenditööstusest tekkivad tahked jäätmed on Eesti teine oluline jäätmeallikas. MJP lendtuhk loetakse ohtlikuks jäätmeteks ja praegu ei ole Eestis selle jaoks käitlemisviisi. Suured CO_2 emissioonid ja tööstuslike tahkete jäätmete kogused on ühed tõsisemad keskkonnaprobleemid, millega Eesti praegu silmitsi seisab.

Käesoleva uuringu eesmärgiks oli anda meetod põlevkivi-, MJP ja tsemendisektorist tekkiva CO_2 ja tahkete jäätmete utiliseerimiseks, keskendudes keemilistele, tehnoloogilistele ja majanduslikele aspektidele. Kasutati kiirendatud karboniseerimise tehnoloogiat kombinatsioonis granuleerimisega, et saada CO_2 keskkonnas kõnealustest tahketest jäätmetest ehitusmaterjali, arvestades jäätmete toodanguks muutmise kontseptsiooniga. Lisaks anti teoreetiline hinnang MJP lendtuha kiirendatud karboniseerimisele. Hinnati väljapakutud stsenaariumide investeeringutulukust, viies läbi kulude ja tulude analüüsi.

Tulemused näitasid, et põlevkivi-, MJP ja tsemendisektorist tekkivad tuhajäätmed on sobivad sorbendid CO_2 sidumiseks kiirendatud karboniseerimismeetodil. Jäätmete CO_2 sidumise võime sõltub peamiselt vaba lubja ja kaltsiumsilikaatide sisaldusest. Segude koostis mõjutas oluliselt CO_2 sidumist, tekkiva granulaadi mehhaanilisi näitajaid, leostusomadusi ning materjali mikrostruktuuri ja morfoloogiat. Üldiselt andsid erinevate jäätmete segud (st MJP tuha lisand) tugevama granulaadi kui põlevkivituhk üksi. Lisaks oli graanulites esinevatel ja väljalekkivatel klooriühenditel negatiivne mõju graanulite veetaluvusele. Leiti, et karboniseerimisprotsess vähendab tõhusalt leovee pH-taset ja elektrijuhtivust. Lisaks vähendas KKT granuleerimise protsess oluliselt tsingi liikuvust. Kokkuvõttes: selleks, et toota keskkonnaohutuid ehitusmaterjale, tuleb ohtlikke MJP jäätmeid kombineerida keskkonnasõbralike või vähem ohtlike tööstuslike kõrvalsaadustega, nt põlevkivituhaga.

Põlevkivi-, MJP ja tsemendisektorist tekkivate tuhajäätmete stabiliseerimiseks CO_2 kasutamise investeeringutulukuse analüüs näitas, et investeeringust võib tulla eratulu, kui utiliseerimise protsessis kasutatakse ainult MJP tuhka, samas kui eratulu ei pruugi

tulla, kui kasutatakse eelkõige põlevkivituhka. Samas tuleb pöörata tähelepanu ka ühiskondlikule kasule , st majandusliku keskkonna halvenemise vähendamisele, heaolu tõstmisele, kliimamuutuse leevendamisele ja teistele seonduvatele ühiskondlikele kasudele.

Selle uuringu tulemused aitavad sulgeda energia- ja tsemendisektori jäätmetsükli, saavutamaks riiklikud ja rahvusvahelised eesmärgid jäätmete taaskasutamise edendamisel, jäätmete ladustamise vähendamisel ja kliimamuutuse leevendamisel, et tagada kestlik tulevik.

Appendix A. Publications

PAPER I

Berber H, Frey R, Voronova V & Koroljova A (2017) A feasibility study of municipal solid waste incineration fly ash utilisation in Estonia. Waste Management & Research 35: 904–912.

Original Article

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A feasibility study of municipal solid waste incineration fly ash utilisation in Estonia

Hakan Berber[1], Ruedi Frey[2], Viktoria Voronova[1] and Arina Koroljova[3]

Abstract

The purpose of this paper is to discuss the alternative environmental management options for the utilisation of municipal solid waste (MSW) incineration fly ash (FA), which is generated at Iru Power Plant where MSW is incinerated in Estonia. To determine sustainable and economically feasible environmental management options for MSW incineration FA in Estonia, CO_2 sequestration with a further carbonation process was examined. A partial Cost & Benefit Analysis has been conducted to compare the carbonation process to the current situation. Two carbonation options were developed. Option 1 is to use carbonated FA in any other processes based on the waste-to-product principle. Option 2 is to send carbonated FA to the non-hazardous landfill in Tallinn, Estonia. Important parameters, such as Net Present Value (NPV), Internal Rate of Return (IRR), Benefit–Cost Ratio (BCR) and Break Even Point (BEP), have been calculated for carbonation options and the current case. In addition, a sensitivity analysis has been conducted to examine its robustness. The results showed that the best option is carbonation Option 1 with NPV of 9,209,662 EUR, IRR of 43%, BCR of 2.63 and BEP between 2018 and 2019. Both Options 1 and 2 constitute more sustainable and environmentally friendly management options compared to the current situation. It can be concluded that this preliminary feasibility study showed that running a carbonation plant may be profitable and sustainable for Estonia. Currently, there is no treatment technology for MSW incineration FA in Estonia and FA is sent to a neighbouring country for further utilisation. This is the first study to demonstrate FA management options with economic and environmental benefits.

Keywords

Municipal solid waste incineration, CO_2 sequestration with further carbonation, Cost & Benefit Analysis, fly ash utilisation

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Introduction

The increasing amount of municipal solid waste (MSW) is a worldwide environmental concern. Traditionally, landfilling had been the most preferred option for MSW management in Eastern Europe. In recent times, however, MSW incineration has been extensively used as an alternative to landfilling. Incineration can drastically reduce the mass and volume of the MSW with a remarkable energy recovery.

In Estonia, there is one MSW incineration plant, which is located in Iru village, Maardu. MSW is mainly treated in this incineration plant in addition to the remnants of landfill disposal after recycling and reuse. In 2013, Eesti Energia AS began to operate an up-to-date waste to energy (WtE) unit to produce heat and electricity by means of MSW incineration at Iru Power Plant. The Iru unit can convert 85% of the energy in waste into electricity and heat. Also, this new unit has an annual capacity of 220,000 tonnes of waste incineration. It allows Estonia to use up to 70 million m^3 less natural gas every year (Eesti Energia AS, 2015). Due to the Iru incineration plant, landfilling on a large scale has ended in Estonia.

The final residues from waste incineration include boiler ash (particulate matter carried over from the furnace and removed from the flue gas without the injection of sorbents) and Air Pollution Control (APC) residues, aside from bottom ash (BA) (Alba et al., 2016). Boiler ash and APC residues are generally taken together as an output from MSW incineration plants. Therefore, the mix of boiler ash and APC residues is termed as fly ash (FA) in this study. However, FA as a solid residue after the MSW incineration process is classified as a hazardous waste under code 19 01 07 in the European Waste Catalogue (ECD, 2000) and needs to be appropriately treated. The ultimate difficulty of MSW incineration FA treatment is that it usually includes metal oxides (CaO, SiO_2 MgO, Al_2O_3, etc.), water-soluble salts (NaCl and KCl), heavy metals (Cd, Zn, Pb, Hg, Cu, Cr and Ni) and organic pollutants (polychlorinated

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dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)). Anna Bogush et al. (2015) indicated that hazardous pollutants, especially Zn (0.098–0.73 wt.%) and Pb (0.05–0.2 wt.%), as well as As, Cd, Cu, Mo, Sb, Sn and Se, are enriched in all the United Kingdom WtE APC residues in addition to Ca-bearing phases, such as calcite ($CaCO_3$), anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), lime (CaO) and soluble salts, such as NaCl and KCl. The presence of lime (CaO) gives FA a high alkalinity, which leads to high leachability feature in landfills. Le Forestier and Libourel (1998) pointed out that the high chlorine content of FA is primarily due to the incineration of plastics, for example, polyvinyl chloride (PVC). Wang et al. (2001) noted that the Cl content in FA should be less than 0.2 wt.% to comply with the requirement of the solidification/stabilisation (S/S) method, for example, carbonation. Chlorine salts are soluble without difficulty on a landfill site where they leaches out a material that leaves a sponge behind. In addition, the leach-out brine is a transport medium for pollutants when the pH is rather alkaline. Finally, heavy metals and organic pollutants need to be treated before spreading into the environment.

These aspects make MSW incineration FA management one of the most important environmental concerns regarding the incineration of MSW. In order to utilise MSW incineration FA and lessen its environmental impact, there are up-to-date treatment processes that include separation processes, S/S processes, thermal methods and some other methods (Quina et al., 2008; Reijnders, 2005). Some of the preferred FA management options seem to be both separation processes with CO_2 sequestration with a further carbonation process and the usage of FA as a raw material in any other industry as a S/S process. On the other hand, sintering or vitrification as a thermal treatment is rather costly. The residue after thermal treatment is even more hazardous than the thermally untreated FA (Ecke, 2003; Jiang et al., 2013; Xiaomin Li et al., 2007). The washing process as a separation process eliminates water-soluble salts and heavy metals (Chimenos et al., 2005; Francois and Criado, 2007; Nzihou and Sharrock, 2002; Zacco et al., 2014). Moreover, Nowak et al. (2012) pointed out that a significant amount of heavy metals and chloride could be removed by using $MgCl_2$ as a thermal treatment. Furthermore, Lima et al. (2012), Pedersen (2002) and Pedersen et al. (2005) showed that the electrodialytic remediation method could moderately eliminate Pb, Cu, Zn, Cd and Cr. Zacco et al. (2014) drew attention to the fact that heavy metal leachability could be lowered by the incorporation of FA into cementitious mixtures.

In Estonia, there is no current treatment technology for FA generated at Iru Power Plant. FA has been sent to a neighbouring country for further utilisation. However, there have been numerous researches on the utilisation of FA from the oil shale power plants in Estonia. It was reported that the main ash flows from pulverised firing (PF) and the circulating fluidised bed (CFB) could be utilised (Raado et al., 2014; Uibu et al., 2015a, 2015b; Velts et al., 2011, 2013). Apparently, the lack of treatment technology for MSW incineration FA comprises an environmental and economic burden for Iru Power Plant. Therefore, an innovative utilisation process is required as an alternative management option to sending it to a neighbouring country.

This paper studies CO_2 sequestration with a further carbonation process as an alternative management option for MSW incineration FA. In this paper, the main emphasis was on the economical assessment. A partial Cost & Benefit Analysis (CBA) has been conducted to compare the application of the carbonation process with the current situation. Moreover, the environmental benefits of the carbonation process are discussed.

Materials and methods

In this preliminary assessment, the analytical framework of CBA suggested by Boardman et al. (2006) was used. Originally, they proposed a nine-step analytical framework. However, this study used a six-step framework, as described below. This partial CBA was conducted at the discount rate of 0.04 for a 10-year period. For each scenario, the Net Present Value (NPV), Internal Rate of Return (IRR), Benefit–Cost Ratio (BCR) and Break Even Point (BEP) were calculated. As a last step, a sensitivity analysis was performed in order to examine the robustness:

1. specify the set of alternatives and the base case;
2. identify benefits and costs;
3. monetise and quantify costs and benefits;
4. find out the discount rate, NPV, IRR and BCR;
5. sensitivity analysis;
6. final recommendation.

Specification of an alternative and the base case scenario

In the CBA, it is crucial to specify a well-advised number of alternatives against the base case scenario. This is because it may be rather difficult to conduct a detailed evaluation within many courses of action.

In this paper, CO_2 sequestration with a further carbonation process has been chosen as an alternative against the base case scenario.

Identification of benefits and costs for monetisation

The base case scenario. In the WtE unit at Iru Power Plant, there are two types of residues other than BA: these are boiler ash and solid waste residues from APC.

Boiler ash is gathered from a stack placed in the boiler and subsequently delivered into a silo with the capacity of 75 m^3. In this silo, it is kept for approximately four days. An approximate annual maximum quantity is 3700 tons. The main elemental analysis showed that the boiler ash includes 31.9% SiO_2, 29.8% CaO, 7.83% Al_2O_3 and 3.79% Fe_2O_3. Due to the existence of lime, it is highly alkaline and the pH was determined as 12.66. Moreover, the main heavy metals were as follows: 19 mg kg^{-1} of Cd, 240 mg kg^{-1} of Cr, 350 mg kg^{-1} of Cu and 600 mg kg^{-1} of Pb. Also, the chloride content was measured as 28,000 mg kg^{-1}.

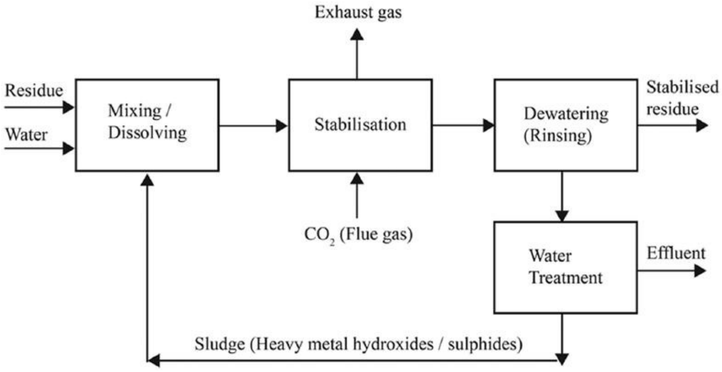

Figure 1. Block diagram of the carbonation process.

A semi-dry management system of combustion gases is used at Iru Power Plant. The APC system consists of a reactor and one baghouse filter. Solid residues are collected from both the reactor and the baghouse filter and delivered to the residue silos with a capacity of 120 m^3. The approximate annual maximum quantity is 7200 tons. The main elemental analysis indicated that the APC residue includes 8.52% SiO_2, 43.6% CaO, 2.83% Al_2O_3 and 0.967% Fe_2O_3. The pH of this residue was 12.39. Furthermore, the main heavy metals were as follows: 0.01 mg kg^{-1} of Cd, 1.1 mg kg^{-1} of Cr, 1.7 mg kg^{-1} of Cu and 470 mg kg^{-1} of Pb. The chloride content was 159,000 mg kg^{-1}.

In this paper, the mixture of boiler ash and solid residues from APC is termed as FA. The FA produced at Iru Power Plant is loaded into the trucks and delivered to a neighbouring country. The only costs for the base case scenario are transportation and treatment costs. In the base case scenario, no benefits could be monetised.

CO_2 sequestration with a further carbonation process. The carbonation process is one of the state-of-the-art stabilisation methods for FA. Several recent studies have investigated the carbonation process in detail (Cappai et al., 2012; Ecke, 2003; Xiaomin Li et al., 2007).

Naturally, the carbonation process occurs as a result of weathering processes where the substance makes contact with atmospheric CO_2. However, the natural carbonation process for FA stabilisation on a practical level is rather slow and is a long-term process. The accelerated carbonation process is a solution for reducing the required time for completion of the carbonation process. Jiang et al. (2013) pointed out that incineration flue gas could be used as CO_2-rich gas for the carbonation process. According to their research, SO_2 emissions inside the flue gas reduce the uptake and sequestration rate of CO_2; as a result, SO_2 blocks the pores of FA and decreases the ability of FA for the sequestration process. In addition, according to Xiaomin Li et al. (2007), the FA could combine with 7–10% w/w of carbon dioxide during the carbonation process. FA has a highly alkaline feature because it includes high concentrations of lime (CaO) and calcium hydroxide ($Ca(OH)_2$), resulting in a high potential for leaching. Xiaomin Li et al. (2007) showed that the original pH of raw FA reduced from 12–12.5 to around 7–10 thanks to the accelerated carbonation process.

The washing process takes place within the accelerated carbonation process to eliminate soluble chloride, sulphate and fluoride. Many authors have reported that the washing process with water can remove soluble salts and soluble heavy metals (Astrup, 2008; Wang et al., 2010; Xiaomin Li et al., 2007). In a detailed study, Wang et al. (2001) experienced 97% of chloride removal efficiency at the liquid/solid ratio of 10. In addition, Jianga et al. (2009) noted that up to 72.8% of Ca, Na, K and Cl was removed at the 10:1 liquid/solid ratio and approximately 12.3% removal was accomplished for Cr.

Figure 1 shows a block diagram of the carbonation plant. For this plant setup, the goal is to test the process at a technical scale with continuous operation at Iru Power Plant.

The mass balance for the carbonation process is presented in Figure 2.. This figure is the base for the calculation of the operational cost in addition to the maintenance cost. In this Dansk Restprodukt Hantering (DRH) carbonation technology, firstly it is ensured that the water and FA are mixed properly. Also soluble salts, heavy metals and other soluble molecules are dissolved. Then, the carbonation reaction occurs in the second place where CaO reacts with CO_2. In this step, the stabilisation of FA occurs. Heavy metals are stuck in $CaCO_3$ and the alkalinity feature of FA decreases. After rinsing process, the stabilised FA is collected. Moreover, the sludge from the wastewater treatment process is pumped back to the process. The effluent from the wastewater treatment process could be discharged into the municipal sewerage system. The DRH process enables that leaching from treated MSW incineration FA is generally below the European Union (EU) acceptance criteria and could be landfilled in non-hazardous landfills (Astrup, 2008).

To implement this alternative at Iru Power Plant, a carbonation plant should be constructed, although this requires significant investment. During the operation of the plant, some additives and power will be combined with the operation costs. Furthermore, regular maintenance is needed throughout the operation. Also, three employees will be hired to run the plant.

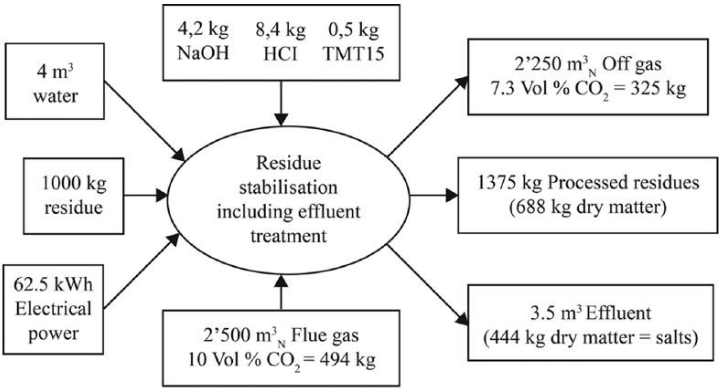

Figure 2. The mass balance of the Dansk Restprodukt Hantering carbonation process.

Table 1. Costs and benefits of Options 1 and 2.

Costs for Option 1	Costs for Option 2	Benefits for Options 1 and 2
Investment cost	Investment cost	Reduction in treatment cost
Operation and maintenance cost	Operation and maintenance Cost	Reduction in transportation cost
Job creation cost	Disposal cost	
	Transportation cost (to landfill site)	
	Job creation cost	

Upon implementation of this technology, no treatment or transportation costs will be paid to the neighbouring country. These reductions are a benefit to Iru Power Plant in monetary terms.

After FA is stabilised by the DRH carbonation process, there are two options for managing the stabilised FA. Option 1 is to use it in any other process based on the waste-to-product principle. For instance, treated FA could be used in concrete, cement production, backfilling of oil shale mines, agriculture or asphalt production (Aubert et al., 2006; Saikia et al., 2007; Wang et al., 2010). Moreover, carbonated FA could be used in concrete blocks and as a horticultural growing medium in green roof systems (Bertos et al., 2004). Option 2 is to send the carbonated FA to a non-hazardous landfill near Tallinn city. The costs and benefits for Options 1 and 2 are shown in Table 1. In Option 1, no landfilling cost is imposed. However, further research is required to determine a process that would be economically and technically feasible for carbonated FA at Iru Power Plant. Option 2 involves transportation and disposal costs. Carbonated FA will be transported from Iru Power Plant to the landfill area near Tallinn.

Description of the discount rate, NPV, IRR and BCR

In a CBA, the criterion for decision-making is based on the NPV, IRR and BCR. Each value is compared to those of other courses of action to determine the best option.

The NPV is used to calculate the yearly benefit and cost components into a present value. This evaluation reveals whether the sum of the discounted gain is higher than that of the discounted losses. In a CBA, discounting is used to convert all future costs and benefits into present-day values, where the time value of money is taken into account. It is important to underline that discounting is not the same as inflation. Primarily, the alternative with the highest NPV is preferable. A general formula suggested by Boardman et al. (2006) for the calculation of the NPV is as follows

$$NPV = -K + \sum_{t=0}^{n} \frac{B_t - C_t}{\left(1 + p_x\right)^t} \tag{1}$$

In this equation, K refers to the initial capital investment for the first year; B and C are the benefits and costs in year t, respectively; and p_x denotes the discount rate.

The IRR is a discount rate at which a project's NPV is equal to zero. If the IRR is greater than the discount rate, the NPV is positive, which demonstrates that the project is economically feasible. The IRR is used to assess the attractiveness of a project. The formula for the IRR, as suggested by Boardman et al. (2006), is given as follows

$$0 = -K + \sum_{t=0}^{n} \frac{B_t - C_t}{\left(1 + \pi\right)^t} \tag{2}$$

Here, π represents the IRR and the other symbols are as described as in the NPV formula.

The BCR is a ratio that should be larger than or equal to zero, which fundamentally means that the NPV of benefits is superior to that of costs to gain a profit. The general formula, as suggested by Boardman et al. (2006), is as follows

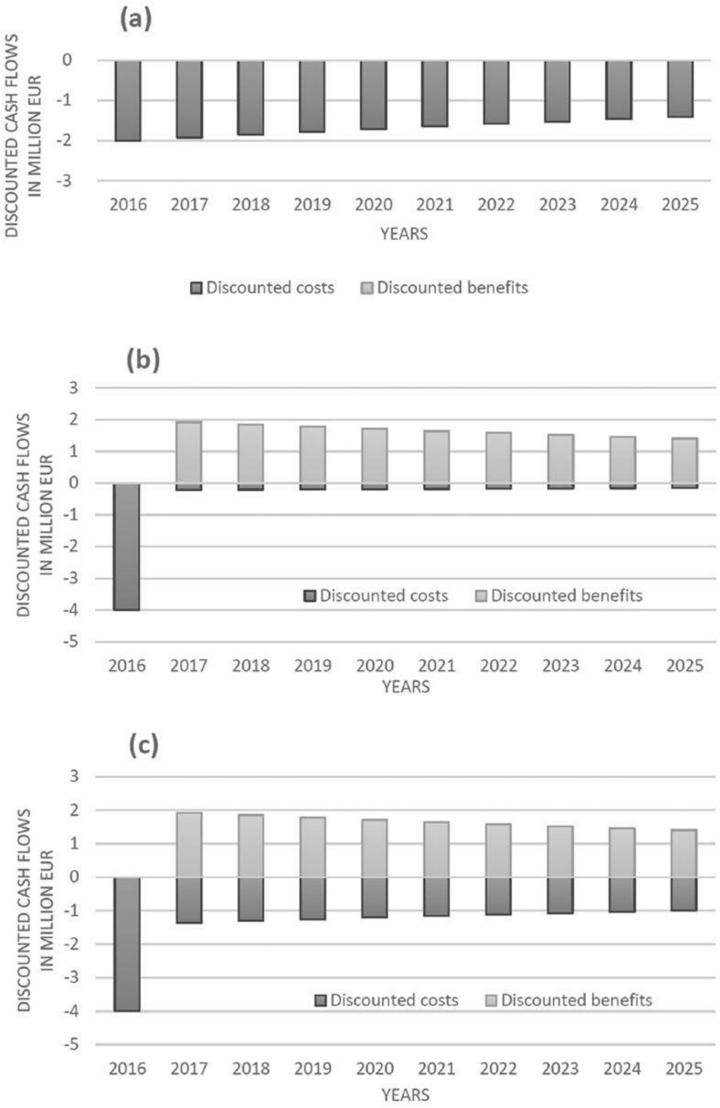

Figure 3. Discounted cash flows for the base case (a), Option 1 (b) and Option 2 (c).

$$BCR = \frac{\sum_{t=0}^{n} \frac{B_t}{\left(1+p_x\right)^t}}{\sum_{t=0}^{n} \frac{C_t}{\left(1+p_x\right)^t}} \tag{3}$$

Results and Discussion

Monetisation of costs and benefits with NPV, IRR and BCR

The base case scenario contains only one monetised cost composed of the treatment and transportation costs of FA. As a result, no monetised benefit is gained. The scenario involves no changes in the current situation. As was described earlier, annual FA generation at Iru Power Plant amounts to 10,900 tons (Eesti Energia AS, 2015). The treatment and transportation cost for FA is 2,000,000 EUR annually, based on market research. Figure 3(a) presents the discounted cash flows for the period between 2016 and 2025 for the base case scenario. As a result of the calculations, the NPV was found to be −16,870,663 EUR at the end of 2025 under the base case scenario. However, it is unreasonable to calculate either the IRR or the BCR because there is no monetised benefit in the base case scenario.

Firstly, an investment should be made to construct the desired carbonation plant. The investment cost was determined at 4,000,000 EUR. This consists of major equipment, land use, labour costs, transportation and civil infrastructure. The investment includes 1,500,000 EUR for major equipment, such as a mixing

Table 2. Operation cost of the carbonation process with components.

Component	Quantity [per ton FA]	Market price	Cost [per ton FA]	Annual cost
Water	4 [m^3 t^{-1}]	0.026 [€ m$^{3-1}$]	0.106 [€ t^{-1}]	1,155 [€ y^{-1}]
Power	62.5 [kWh t^{-1}]	0.061 [€ kWh^{-1}]	3,812 [€ t^{-1}]	41,550 [€ y^{-1}]
Flue gas	2,500 [m^3 t^{-1}]	–	–	–
NaOH	4.2 [kg t^{-1}]	0.417 [€ kg^{-1}]	1,751 [€ t^{-1}]	19,009 [€ y^{-1}]
HCl	8.4 [kg t^{-1}]	0.075 [€ kg^{-1}]	0.63 [€ t^{-1}]	6,867 [€ y^{-1}]
TMT15	0.5 [kg t^{-1}]	7,121 [€ kg^{-1}]	3,560 [€ t^{-1}]	38,812 [€ y^{-1}]

FA: fly ash.

tank, stabilisation tank, vacuum bet filter, scrubber and flue gas compressor, and excludes pipelines and pumps. The other part of the investment cost is approximately 2,500,000 EUR, which covers land use, labour, transportation and construction costs.

The maintenance cost is determined as 2% of the investment cost. This component includes the replacement of worn parts, such as pH-probes, CO_2 injection nozzles and spear parts. Also, specialists for servicing special parts will be needed as an external cost. Altogether, maintenance costs will amount to 80,000 EUR per year.

The calculated operation cost for the carbonation plant is presented in Table 2. The annual operation and maintenance costs are 107,393 and 80,000 EUR, respectively. Altogether, the annual operation and maintenance costs are 187,393 EUR.

The other cost component is job creation. It was decided to hire three employees during the operation. This number may change depending on the needs and ongoing situation. The relevant cost was taken as 36,000 EUR per year. Moreover, job creation would ensure social benefits, such as an increase of financial security, promotion of higher living standards and trigger of economic activity.

For the carbonation process, a benefit source is the reduction in the current treatment and transportation costs in the base case scenario. This comprises an unspent 2,000,000 EUR per year.

The discounted cash flows under the waste-to-product carbonation scenario (Option 1) are presented in Figure 3(b). From the investment in 2016, no benefit was derived since the FA is still sent to a neighbouring country. From 2017, the carbonation plant with full operation will be in use. The FA will be carbonated and used in different industrial areas as a stabilised product.

At the end of 2025, under Option 1, the NPV, IRR and BCR will be 9,209,662 EUR, 43% and 2.63, respectively. This amount fundamentally represents the NPV of the profit from the loss end of the 10 years compared to the base case scenario.

Under the landfilling carbonation scenario (Option 2), the treated FA will be delivered to Tallinn's landfill, which is 10.8 km away from Iru Power Plant. The cost of transportation by trucks per ton of FA per km is 0.07 EUR. This comprises an annual transportation cost of 11,330 EUR at 14,987 tons of annual carbonated FA. The landfilling fee for stabilised waste is 78.41 EUR per ton at Estonian landfills. The annual disposal cost for carbonated FA is 1,175,131 EUR. Discounted cash flows under Option 2 are presented in Figure 3(c).

At the end of 2025, under Option 2, the NPV, IRR and BCR will be 387,931 EUR, 6% and 1.03, respectively. This indicates that Option 2 has better economical results than the base case scenario.

One of the most important parameters in CBA is the payback period. The payback periods for carbonation under Options 1 and 2 are shown in Figure 4. The figure indicates that the funds expended in the investment will be recouped in less than three years under Option 1 and less than 10 years under Option 2. This point is known as a BEP. Under Option 1, the BEP is prior to 2019. In fact, it may be even shorter in the case of revenue from sales of the treated FA to any other industrial process. In addition, Figure 4 illustrates that the profit from the loss under Options 1 and 2 will increase with time. Figure 4 also shows that it could recoup the funds expended in the investment under both Options 1 and 2 within 10 years.

Furthermore, CBA has been used by several authors in different fields related to environmental engineering. Wang et al. (2016) used CBA to investigate greenhouse gas (GHG) emission reduction in WtE projects in China. They also proposed two different scenarios and pointed out the better scenario with the benefits. In the energy field, Groth and Scholtens (2016) conducted a CBA to compare biomass and natural gas combined heat and power (CHP) projects in Denmark and the Netherlands. They assessed the same projects based on the guidelines in both countries. In addition, Clinch and Healy (2001) used a comprehensive CBA to assess domestic energy efficiency programmes.

Sensitivity analysis

In practice, substantial uncertainties are always likely to be found in calculations in the CBA analysis. The significance of monetised sources may change, which may affect the results in possibly both a positive and negative way.

Firstly, the change of the NPV was discussed depending on the different discount rates. In this study, the optimum discount rate was determined at 0.04. The NPV changes with the discount rates of 0.03 and 0.07 were investigated. In addition, García-Gusano et al. (2016) recommends using a reference value not higher than 4–5% in European countries. Table 3 gives the NPV changes with different discount rates for costs, benefits and the total under both carbonation options and the

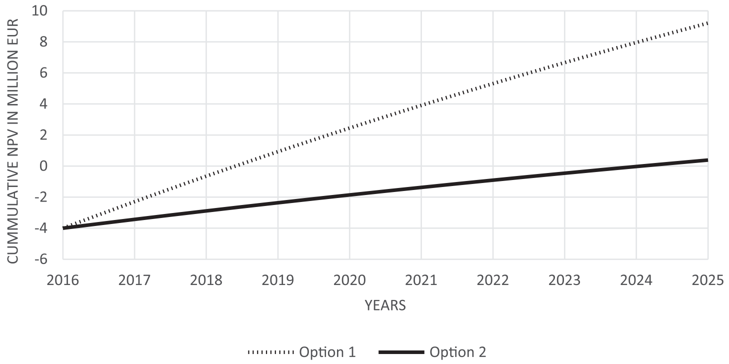

Figure 4. Discounted payback period of Options 1 and 2. NPV: Net Present Value.

Table 3. Discount rates of 3% and 7% compared to 4% base and assumptions altered for the cost source for carbonation options and the base case.

Carbonation Option 1			
Assumptions	*NPV – costs [€]*	*NPV – benefits [€]*	*NPV – total [€]*
$P_x = 3\%$	5,739,362	15,572,218	9,832,848
$P_x = 4\%$	5,661,001	14,870,663	9,209,662
$P_x = 7\%$	5,455,457	13,030,464	7,575,001
20% Cost Increase ($P_x = 4\%$)	5,993,201	14,870,663	8,877,462
20% Cost Decrease ($P_x = 4\%$)	5,328,801	14,870,663	9,541,862
Carbonation Option 2			
Assumptions	*NPV – costs [€]*	*NPV – benefits [€]*	*NPV – total [€]*
$P_x = 3\%$	14,977,277	15,572,218	594,941
$P_x = 4\%$	14,482,732	14,870,663	387,931
$P_x = 7\%$	−13,185,526	13,030,464	−155,062
20% Cost Increase ($P_x = 4\%$)	−16,579,278	14,870,663	−1,708,615
20% Cost Decrease ($P_x = 4\%$)	−12,386,186	14,870,663	2,484,478
Base case			
Assumptions	*NPV – costs [€]*	*NPV – benefits [€]*	*NPV – total [€]*
$P_x = 3\%$	17,572,217	0	−17,572,217
$P_x = 4\%$	16,870,663	0	−16,870,663
$P_x = 7\%$	15,030,464	0	−15,030,464

NPV: Net Present Value.

base case scenario. The total NPV with 7% discount rate under Option 1 still presented a rather high profit. It shows that the NPV would not move below zero in a worst-case scenario. However, the total NPV with a discount rate of 7% under Option 2 was nevertheless minus. This indicates that it cannot be larger than zero in a worst-case scenario.

Secondly, it is important to analyse the change in the sources of costs to see the variations of the total NPV after 10 years. For instance, operation and maintenance costs may vary in the future. Furthermore, transportation or disposal costs may also change in either direction. Therefore, the cost sources are increased and decreased by 20%. Moreover, how the total NPV responds to this change is analysed for the options. Also, the decrease in cost sources will end up with a higher NPV, as desired. Table 3 shows the results for all the scenarios. Since the cost is not high, the change in the total NPV is lowest under carbonation Option 1. As a result, carbonation Option 2 has higher costs and the response to this change was rather high. It was observed that Option 2 had a minus value for a 20% increase in the cost sources. In this case, Option 2 would not be a better economical option than the base case scenario.

An attempt has been made to analyse the alternatives for the changes that are likely to occur over 10 years. The results showed that the total NPVs of the carbonation waste-to-product scenario even showed positive results in a worst-case scenario. Moreover, the change in NPV over the years with different discount rates is not vital.

Environmental benefits of the chosen alternatives

MSW incineration flue gas includes approximately 10–15% CO_2 and it is accepted that it has a substantial contribution to the greenhouse effect (Jiang et al., 2013). Under Options 1 and 2, there will be a noteworthy reduction in CO_2 emissions, namely 169 kg per year. The soluble salts are eliminated from FA through the carbonation process and its hazardousness is reduced. In addition, as presented in Figure 1, the sludge, including heavy metals and sulphides, is recycled back into the process, which prevents the release of heavy metals. The heavy metals presented in untreated FA are stuck in the treated FA due to the carbonation process. In other words, a buffer capacity in the neutral or slightly alkaline range (calcium carbonate) is desired, since it prevents heavy metals from leaching out at a low pH. Moreover, after the carbonation process, the pH of FA is lowered significantly to a neutral or slightly alkaline range, which stabilises the FA. Under Option 1, the carbonated FA becomes a product and will no longer be landfilled, which minimises the environmental burden.

Both Options 1 and 2 are environmentally better FA management options compared to the current situation.

Conclusion

This paper investigates CO_2 sequestration with a further carbonation process as an alternative to sending FA to a neighbouring country. This comprises an economical burden for Iru Power Plant in Estonia. DRH carbonation technology can be a profitable and sustainable solution for this problem.

This paper concludes that the best option for decision-making was Option 1 (the waste-to-product carbonation scenario). The NPV, IRR and BCR values were found to be 9,209,662 EUR, 43% and 2.63 at the end of 2025, respectively. In addition, the BEP was indicated before 2019. In sensitivity analysis, the NPV was still positive under a 20% cost increase or 7% discount rate.

Option 2 (landfilling carbonation scenario) had the NPV, IRR and BCR values as −387,931 EUR, 6% and 1.03, respectively. Over 10 years, it could reach the BEP just after 2024. In sensitivity analysis, a 7% discount rate could not succeed in making the NPV larger than zero. Fortunately, the NPV was calculated at 2,484,478 EUR under a 20% cost decrease.

The results showed that running a carbonation plant under Options 1 and 2 at Iru Power Plant in Estonia may be an economically and environmentally friendly choice compared to the ongoing situation.

It should be emphasised for future work that a comprehensive CBA should be conducted where all elements are taken into consideration. For instance, the price fluctuations of the cost and benefit sources, the layout and capacity of the plant and the depreciation and life time of the plant should be included. Furthermore, CO_2 reduction from the flue gas should be monetised as a benefit source under carbonation options. In addition, the risk and uncertainty associated with the project outcomes should be investigated.

Declaration of conflicting interests

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PAPER 2

Berber H, Tamm K, Leinus ML, Kuusik R & Uibu M (2019) Aggregate production from burnt oil shale and CO_2 – an Estonian perspective. *Oil Shale* 36: 431–447.

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Aggregate production from burnt oil shale and CO_2 – an Estonian perspective

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Abstract. *Estonia's main calcareous industrial waste output, such as burnt oil shale (BOS) from Narva Power Plants (PPs), cement kiln dust (CKD) from AS Kunda Nordic Tsement and municipal solid waste incineration (MSWI) residues from Iru Power Plant (PP), were all tested in a novel mixer-type granulator-carbonator for the production of constructional aggregates, with a focus being placed on the mechanical properties, the* CO_2 *binding ability, and leaching behaviour. The mixtures of wastes after the addition of cement and quarry fines gave aggregates which exhibited satisfactory mechanical and leaching properties for further utilisation. The results of this study could serve as a basic research step towards closing the waste cycle in Estonian energy and cement sectors.*

Keywords: *burnt oil shale, municipal solid waste incineration ash, cement kiln dust, mineral carbonisation, granulation.*

1. Introduction

The largest proportion of all industrial waste in Estonia is generated by the oil shale-based energy sector in the form of oil shale ash [1]. In 2016 approximately seven million tons of ash, according to Eesti Energia AS, was deposited in ash fields [2]. However, the target is to increase the utilisation of ash in the nearest future [3]. The main application areas for burnt oil shale (BOS) include the production of building materials (as an aggregate in cement, or autoclaved aerated concrete blocks, or as an additive in concrete and dry construction mixtures (EVS 927:2017 [4])), road and port construction, neutralisation of acidic soils, and as a binder of CO_2 and sulfur that are released during energy production [5]. The ash that is produced by the cement industry and the municipal solid waste incineration (MSWI) field generate another significant

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waste stream [1]. Berber et al. [6] showed that accelerated carbonation technology could be an economically sound solution for stabilising the MSWI fly ash from Iru Power Plant (PP). However, currently the harmful ash from Iru PP cannot be directly disposed of in the landfill but must be transported to a hazardous waste management company [7]. Thermal power plants (PPs) and cement plants are also amongst the biggest CO_2 emitters [2, 8, 9]. Closing the waste loop requires the use of millions of tons of ash in which BOS constitutes the major proportion. By applying the agglomeration process, such waste could be turned into a product to be used either in the construction or agricultural industry. Previous practice has shown that BOS and cement kiln dust (CKD) could be utilised as liming agents for acidic soils [10–12]. However, in practice, the utilisation of these forms of waste is limited in Estonia.

Alternatively, the above waste could be utilised to produce construction aggregates by using the accelerated carbonation-based solidification [13]. Specifically, Gunning et al. [13] showed that the key properties of the carbonated aggregates that were being produced by the above-mentioned technology were similar to those of lightweight aggregates (LWA) which were available in the UK in 2009. The production of artificial carbonated aggregates has been demonstrated by Carbon8, a spin-off company of the University of Greenwich in England which uses mineral carbonation treatment to produce artificial aggregates from several residues, such as MSWI ash, quarry fines, etc., for further utilisation in the manufacturing of carbon neutral building blocks (CO_2, sand, and cement) by Lignacite in the UK [14].

The current study was carried out in light of the targets set in the Estonian National Waste Management Plan 2014–2020 [15] and the Estonian Environmental Strategy 2030 [3]: 1) to promote waste recovery; 2) to reduce by 2030 waste dumping by 30% in addition to alleviating the environmental hazard posed by generated waste; 3) to abate greenhouse gas emissions and save resources. Therefore, this study could be a crucial step in the process of achieving all of the main targets by promoting waste recovery and abating CO_2 emissions from the power and cement sectors, as well as from MSWI plants, and, by this means spare raw materials and endorse the waste-to-product (WtP) approach.

All in all, this work could be heralded as the first study in Estonia of the variety of industrial waste, including BOS waste from Narva PPs and shale oil production (Enefit 280), CKD from AS Kunda Nordic Tsement and MSWI air pollution control (APC) residue from Iru PP, for the production of construction aggregates. This study focused on a novel mixer-type granulator-based technology, which permitted the carrying out of hydration, carbonation and granulation steps in the same reactor. The mechanical properties of produced aggregates, the CO_2 binding ability of the above wastes and reduction of the environmental hazard caused by them were covered as well. The specific aim was to study the applicability of this method.

2. Materials and methods

2.1. Materials

Different solid wastes from power and cement plants were utilised in order to produce construction aggregates via the carbonation-based solidification technique. The BOS1 and BOS2 markers represent the ash that is produced in electrostatic precipitators and BOS5 stands for total ash silo in the circulating fluidised bed boilers of Narva PPs. The BOS3 sample was collected from an SO_2 removal system (Novel Integrated Desulphurisation, Alstom Power) that is part of a pulverised firing boiler. The BOS4 sample was collected from Enefit280 units used in shale oil production. The solid waste from other industries, i.e. MSWI APC residues from Iru PP and CKD from Kunda Nordic Tsement, were also tested. The additives – Portland cement (CEM I, 42.5R) and quarry fines – were provided by AS Kunda Nordic Tsement.

2.2. Methods

The materials under study were analysed using X-ray fluorescence spectroscopy (XRF, Rigaku Primus II) and quantitative X-ray diffraction (XRD, Bruker D8 Advanced) at the Institute of Geology, University of Tartu (UT). The contents of free lime (fCaO) (the ethylene glycol method [16]), sulfate [17] and total carbon (TC) (Electra CS – 580 Carbon/Sulfur Determinator) were determined. In addition, the BET specific surface area (SSA) and the particle size distribution were determined using a Kelvin 1042 sorptometer and a Horiba laser scattering particle size distribution analyser LA-950, respectively.

Figure 1 shows the experimental setup. The hydration, carbonation and mixing with the additives (step 1), followed by granulation (step 2), were all carried out by Eirich GmbH in a Co EL1-type intensive mixer/granulator operated under different regimes. In the first step, the rotational speed of the rotor tool was set at 3000 RPM for intensive mixing, in a clockwise direction, whereas it was set at 610 RPM in an anti-clockwise direction throughout the second step of granulation. The mixing pan was operated at slow speed (85 RPM) throughout the experiment. Granulation is the agglomeration of powdered material particles into granules of a specific size and spherical shape. The granules structure is formed either by physical forces or through

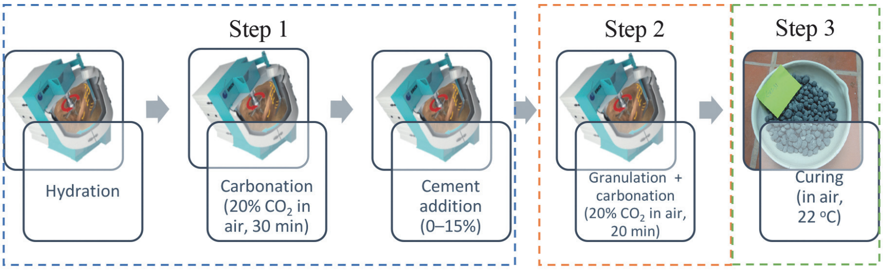

Fig. 1. Experimental setup.

the use of binders. The granulation process is controlled by the physicochemical properties of the powdered material, and by moisture content, particle size, operating conditions, and process parameters such as the rotary speed of the granulator [18, 19]. The waste was treated individually as well as in the composition of mixtures (using 0–15% cement and 0–30% quarry fines as additives), under different operating regimes, by varying the solid-to-liquid ratio, the rotation speed, the CO_2 content in model gas, residence time, curing conditions, etc. It is important to note here that the CO_2 concentration in the model gas was determined as being at 20% since in the cement industry's typical flue gas stream, it varies between 14 and 33% [20]. The experiment plan and process parameters are given in Table 1.

Table 1. Experimental plan and process parameters

Granule	Initial waste material	OPC, %	Quarry fines, %	L/S, w/w
gBOS1	BOS1	5	0	0.45
gMIX1-0	4BOS1+APC+CKD mixture	0	0	0.30
gMIX1-9		9	0	nd
gMIX1-10-q		10	30	0.22
gBOS2	BOS2	5		0.42
gMIX2-0	4BOS2+APC+CKD mixture	0	0	0.38
gMIX2-5		5	0	0.32
gMIX2-10		10	0	0.30
gBOS3	BOS3	5		0.23
gMIX3-15	4BOS3+APC+CKD mixture	15	0	0.17
gMIX3-5-q		15	30	0.16
gMIX3-10-q		10	30	0.15
gMIX4-5	4BOS4+APC+CKD mixture	5	0	0.25
gMIX4-10		10	0	0.25
gMIX4-10-q		10	30	0.18
gBOS5	BOS5	5		0.34

OPC – ordinary Portland cement; nd – not determined; 4BOS+APC+CKD stands for 4:1:1 proportion.

The granules were dried in a thermostat for three hours at 105 ºC and analysed for TC and free lime content as the main indicators of the carbonation process. The efficiency of the carbonation process was described by the CO_2 binding degree (BD_{CO_2}). BD_{CO_2} shows how much of the theoretical CO_2 binding capacity is being utilised (Eq. (1)):

$$BD_{CO_2} = \frac{CO_2\ granules}{CO_2\max_{ash} + CO_2\max_{cement} + CO_2\max_{quarry\ fines}} \times 100, \qquad (1)$$

where $CO_{2granules}$ is the analytically determined CO_2 content of the granules, CO_{2max} is the maximum possible CO_2 content of the granulated mixture of ashes, cement and quarry fines in percentage terms, according to Equation (2):

$$CO_2\max = \frac{X + CO_2^{\,i}}{100 + X} \times 100, \qquad (2)$$

where X is the CO_2 uptake capacity of the initial material when considering free lime, wollastonite, belite, merwinite, alite, and Ca-aluminate, and $CO_2^{\,i}$ is the carbon dioxide content of the initial materials.

After one week of curing at room temperature (about 22 ºC) the granules were tested for mechanical properties such as fractional composition and compressive strength by using the Brookfield CT3 25K texture analyser according to CEN-EN 1097-11:2013 [21]. The apparent density was measured using a Mettler Toledo density kit AX204 according to EVS-EN 1097-6:2016 [22].

The leaching tests were carried out according to European standard EN 12457-2:2002 [23]. The leachate pH was determined using a Mettler Toledo SevenGo pH meter and the electrical conductivity was determined employing a Mettler Toledo SevenGo Duo Pro. The composition of ash leachates was determined according to DIN EN ISO 10304-1/-2(D19/20, E29) [24, 25].

Environmental analyses were carried out using the methods of DIN EN 16171 [26], DIN EN ISO 10523 [27], DIN EN 27888 (C8) [28], DIN EN ISO 17294-2 (E29) [29] and DIN EN ISO 10304-1 D20 [24] by GBA Gesellschaft für Bioanalytik mbH.

3. Results and discussions

Burnt oil shale (BOS1–BOS3) and APC residue contained lime and/or portlandite as the main phases that reacted with CO_2, to form calcium carbonate (Fig. 2). In addition, APC residue contained water soluble chloride compounds, such as halite, sylvite and calcium hydroxide chloride, which, due to their expansive behaviour that causes the development of both pores and cracks in the microstructure, might be of concern for aggregates produced [30]. Calcium appeared mainly as calcite in CKD and BOS4 samples. Silica was found in samples as quartz and K-feldspar, as well as secondary silicates, which could also bind CO_2. The selected physico-chemical characteristics of the materials are provided in Table 2.

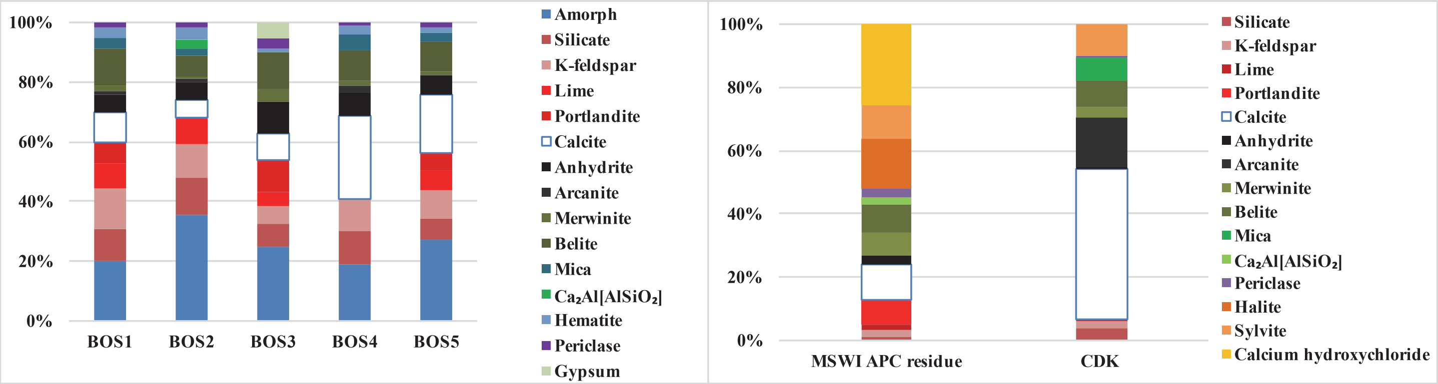

Fig. 2. The phase composition of BOS, MSWI APC residue and CKD.

Table 2. Physico-chemical characteristics of industrial waste materials

Oil shale ashes from Narva PPs and Enefit280					
Initial sample	d_{mean}, µm	SSA, m^2/g	fCaO, %	CO_2, %	S_{SO_4}, %
BOS1	20.99	4.75	12.00	5.31	1.93
BOS2	43.58	3.08	9.76	3.79	2.20
BOS3	14.86	1.27	8.56	4.26	2.42
BOS4	36.48	4.24	0.36	16.83	2.26
BOS5	39.51	3.74	11.63	12.95	2.22
Cement kiln dust and OPC from AS Kunda Nordic Tsement					
CKD	34.33	4.16	2.01	20.30	2.49
OPC	16.76	1.76	2.54	1.80	1.41
Quarry fines	–	4.26	0.03	41.12	–
MSWI APC residue from Iru PP					
APC residue	40.42	7.88	10.02	6.35	2.49

OPC – ordinary Portland cement; "–" represents no data.

The results of the leaching analyses for the initial waste samples are given in Table 3. In the case of APC residue from Iru PP as the most hazardous sample in this study, the leachability of chlorides, Pb and total dissolved solids (TDS) exceeded the limits for hazardous waste, and Hg, Cr, Zn, Cu, Mo and Ba surpassed the target values [31]. The CKD from Kunda Nordic Tsement was characterized by the high leachability of chlorides, sulphates, fluorides, Pb, Cr and Mo. The contents and mobility of heavy metals in other BOS samples were found to be similar.

The experiments indicated that CO_2 uptake as well as the mechanical properties of BOS types, CKD and MSWI APC residue-based aggregates could differ across a very wide range. The CO_2 uptake was mainly attributed to the relatively high content of free lime (10–15%) in BOS1, BOS2, BOS3 and BOS5 ashes from Narva PPs and the MSWI APC residue from Iru PP. At the same time, the fCaO content was negligible in the CKD from Kunda Nordic Tsement and BOS4 ash from shale oil production, which did not favour CO_2 uptake (Table 2).

Tests indicated that the free lime content was exhausted within thirty minutes under conditions that included a small-range water-to-solid ratio (0.2–0.5 w/w) and a gas flow of 20% CO_2 in air (Fig. 3). The fCaO content

Table 3. The content and mobility of the main ash components

Component	Content						Mobility, %		
	Limit[1]	Limit[2]	Unit, wt	APC residue	CKD	BOS1	APC residue	CKD	BOS1
SO_4			g/kg	74.7	73.8	57.9	19.5	72.10	0.0
Ca			g/kg	271.4	252.3	238.5	27.2	10.5	4.6
K			g/kg	50.6	111.7	15.2	92.1	87.6	18.4
Na			g/kg	40.0	2.1	1.4	91.0	81.0	7.1
Mg			mg/kg	14580	12530	20820	–	–	0.01
Mn			mg/kg	571	696	344	–	–	–
Hg	0.5	10	mg/kg	20	0.18	< 0.1	1.1	–	–
Cd	1	20	mg/kg	70	12	0.45	–	–	–
Pb	50	600	mg/kg	1900	1870	70	36.8	1.2	0.3
Cr	100	800	mg/kg	209	31	37	1.2	12.9	0.2
Ni	50	500	mg/kg	80	18	31	–	–	–
Zn	200	1000	mg/kg	8880	773	< 0.1	1.5	0.1	–
Cu	100	500	mg/kg	681	31	16	0.6	–	–
As	20	50	mg/kg	39	13	25	–	0.1	–
Mo	10	200	mg/kg	22	4,3	14	20.5	58.1	2.1
Ba	500	2000	mg/kg	751	76	176	3.9	7	15.3

Limit[1] – target value for industrial land; Limit[2] – limit value for industrial land (both [31]); "–" represents no data.

remained at a higher level in BOS3, which is a pulverised firing ash that is characterised by lower BET SSA levels (Table 2).

In BOS1, BOS2 and BOS5-based aggregates, a CO_2 binding degree of up to 78–81% was realised with a remarkable reduction in free lime content, whereas the reactivity of gBOS3 towards CO_2 was moderate (52% of BD_{CO2}).

Adding cement to the BOS mixture caused a decrease in BD_{CO2} as the calculation (Eq. (1)) also included the cement minerals as CO_2 binders (Fig. 4). The reason behind this finding could be the following. First, the outer layers that were formed by the addition of cement might have ceased the further

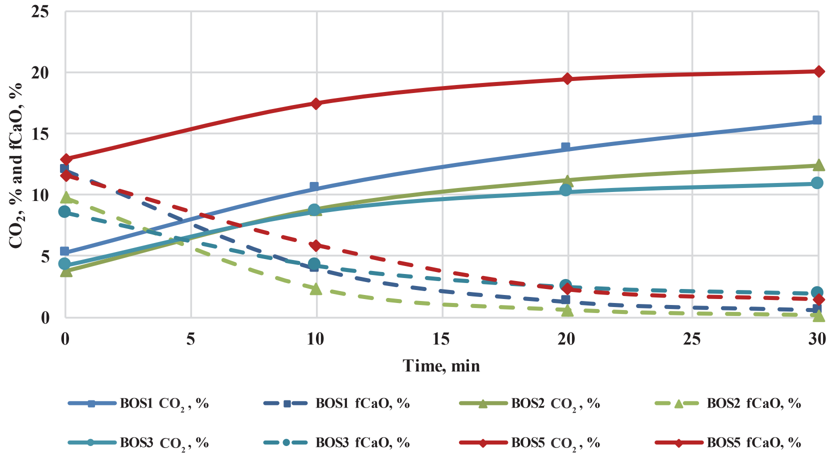

Fig. 3. Changes in CO_2 and fCaO contents in different ashes during the carbonation step.

carbonation of the agglomerated particles in the second step (Fig. 1). Second, the carbonatable compounds inside the cement might not have been exhausted by the 20th minute of carbonation. In addition, the formation of granules decreased further the mobility of reactive species (Ca-silicate phases) owing to that they might have been trapped inside the layers.

The hazardous APC residue and CKD (gMIX1-gMIX4) were included in the mixtures in order to remedy them by capsuling soluble salts (calcium hydroxychloride, halite, sylvite, arcanite (Fig. 1)) and heavy metals into carbonated aggregates. The addition of these forms of waste did not affect the BD_{CO2} (Fig. 4).

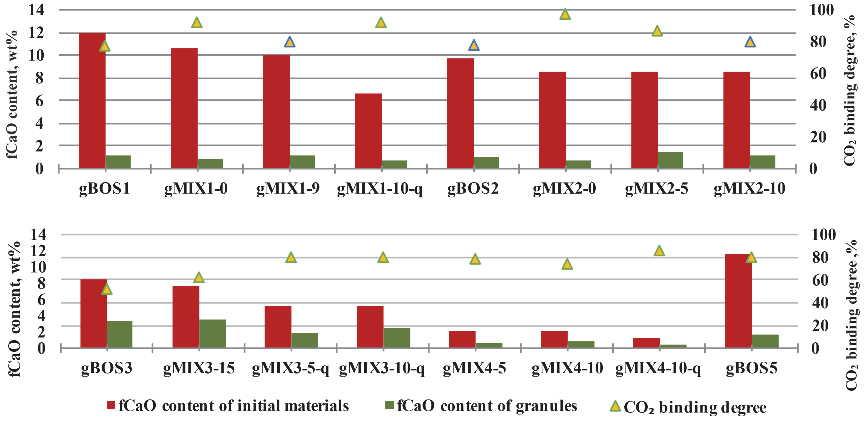

Fig. 4. Changes in free lime content and the resulting CO_2 binding degree of burnt oil shale-based granules.

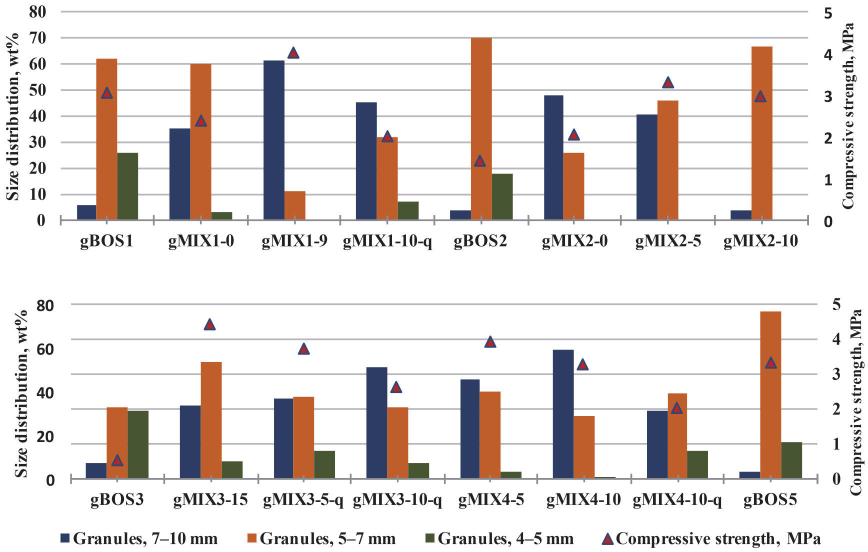

Fig. 5. Compressive strength and size distribution of burnt oil shale-based granules.

A sieve analysis was used to determine the granule size distribution. The results showed that the granules were mainly in the 4 < x < 10 mm size range. The compressive strength values were calculated for the 4 < x < 10 mm granule size range and varied from 0.5 MPa (gBOS3) to 4.4 MPa (gMIX3-15) (Fig. 5). Compared to BOS alone (gBOS1-5), the mixtures (gMIX1-gMIX4) gave stronger granules. BOS3 afforded the lowest compressive strength, which was attributed to its very slow hardening dynamics [32]. Compressive strength was enhanced by adding 5–15% cement; for example, in the case of gMIX1, adding 9% cement led to a 68% increase in compressive strength. The improvement in the compressive strength values could be the result of several mechanisms, such as the formation of a C-S-H-like gel and calcite in the accelerated carbonation conditions [33], the formation of C-S-H stemmed from the reaction of cement with the interior silicate phases of the ash samples [34], as well as pozzolanic reactions [35]. However, the addition of cement was not always proportional to the gain in the granules strength (gMIX2 and gMIX4), meaning that the effect of the mixture composition could be more complicated. The addition of quarry fines as a neutral filler generally decreased the compressive strength of the granules due to the lower amount of the binder in the mixtures [35]. Expressly, the compressive strength values of gMIX1-10-q and gMIX4-10-q were 60% lower than those observed in the same conditions with no inclusion of quarry fines (gMIX1-9 and gMIX4-10).

3.1. The leaching of BOS-based aggregates

Despite the fact that the addition of APC residue and CKD to the mixtures (gMIX1–gMIX4) increased their sulfate content, the leachable content of the sulfates remained well below the hazardous limit (50,000 mg/kg, see Fig. 6). As expected, the high concentration of easily leachable chlorides in the APC residue and CKD (Fig. 2) had a strongly adverse effect on the leaching characteristics of the granules (gMIX1–gMIX4), emphasising the fact that the leachable chloride contents of gBOS1, gBOS2, gBOS3 and gBOS5 were remarkably lower than the limit (20,000 mg/kg). The excessive amount of leachable chlorides and heavy metals in the mixtures could be removed by employing a washing technique [36–38]. Therefore, although the addition of CKD and APC residues rather complicated the leaching behaviour of the obtained granules, the skilful stabilisation of these initially hazardous materials by optimising the mixture composition could provide their rational use.

The addition of cement (5–15%) to the mixtures of different types of waste afforded aggregates that had satisfactory mechanical and leaching properties which were revealed by the decrease of the mobility of heavy metals, chlorides and sulphates. The leaching test indicated that the content of heavy metals such as Hg, Cd, Cr, Ni, Zn, Cu, As, Mo and Ba remained below the hazardous limit in all of the leachates. However, in the case of granules that contained APC residue and CKD, the leachate Pb content slightly exceeded the limit value set for hazardous waste.

One of the main goals in this process was to decrease the alkalinity levels in the initial materials, bringing them down to a pH value less than 11.5 to meet the requirements for inert material (Fig. 7). The granules that were produced from BOS samples (gBOS1, gBOS2, gBOS4, gBOS5) achieved a leachate pH < 11.5. Even though the incorporation of APC residue, CKD and quarry fines in the mixtures played an adverse role in water durability, not to mention the alkaline effect of granules, the leachates for gMIX1, gMIX2 and gMIX4 were characterised by a pH ≤ 11.5. However, the leachates for gMIX3 remained deeply alkaline. Previous studies have also shown that those composites that contained ash from an SO_2 removal system, which were characterised by very

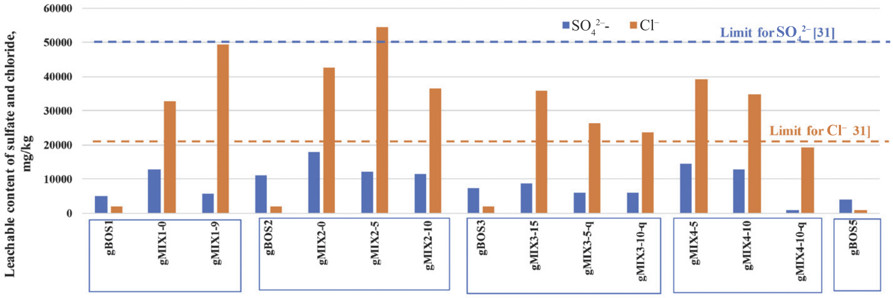

Fig. 6. Leachable contents of sulfates and chlorides.

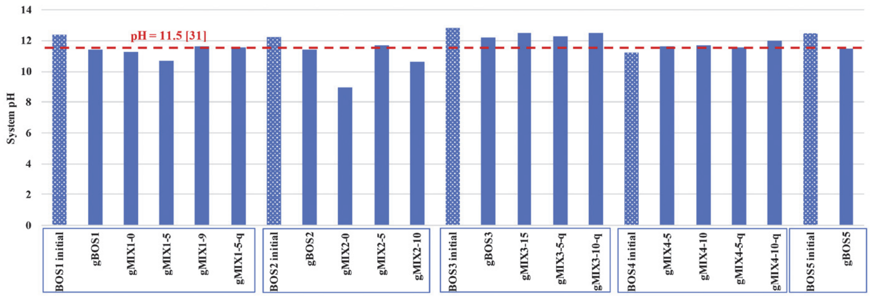

Fig. 7. Leachate pH levels in burnt oil shale samples before (initial) and after accelerated carbonation and granulation.

low compressive strength and water resistance, decomposed in water [32]. The electrical conductivity levels of all types of granules remained below the hazardous limit.

Most of the granules were characterised by an apparent density of nearly 2.1 g/cm^3 (Fig. 8). There was no significant change in apparent density after the leaching test. On the other hand, the compressive strength of the granules was enhanced by leaching. Exposure to water promoted strength development because the delayed reactions might have been inhibited due to a lack of reactive water inside the aggregate [32]. Figure 9 demonstrates the visual features of the granules regarding the shape and the outer surface before and after the leaching test. Most of the granules have a spherical shape without any ”blackberry” structure. After the leaching test, the size of the granules decreased owing to the mass loss, whereas the outer surface became smoother.

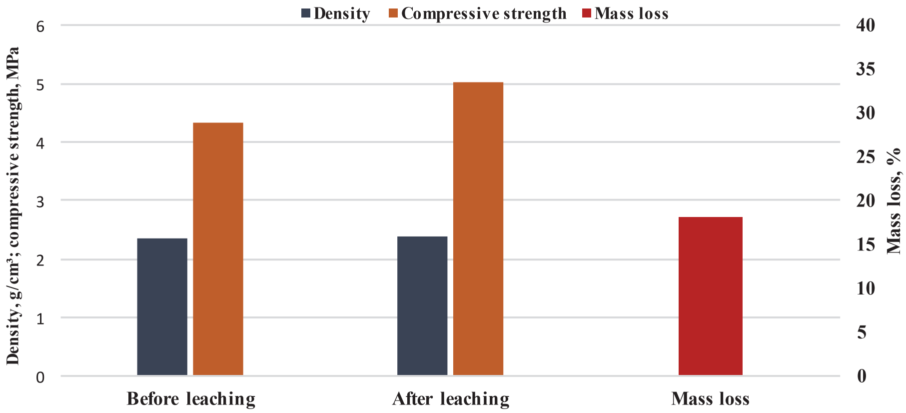

Fig. 8. The density and compressive strength of the granules before and after leaching.

Fig. 9. The granules before and after the leaching test.

4. Conclusions

This paper investigates the possibility of utilising different types of industrial wastes from Estonian oil shale combustion, cement production and municipal solid waste incineration to produce light-weight aggregates as a remedy for the huge volume of CO_2 emissions and vast ash deposits formed in Estonia. Different types of burnt oil shale, cement kiln dust and municipal solid waste incineration air pollution control residues were tested for carbonation-based solidification in a mixer-type granulator. This technique enabled all steps – hydration, carbonation and granulation – to be handled in the same reactor, concentrating on the mechanical properties of the aggregates obtained, including the CO_2 binding ability, and the reduction of the environmental hazard from the respective wastes.

The results showed that the CO_2 uptake was attributed mainly to the relatively high content of free lime (10–15%) in BOS and MSWI APC residues. Ca-silicates such as alite, belite, merwinite, etc. endorsed solidification by also capturing CO_2. Most of the ash and ash blends showed a high reactivity, with CO_2 up to 98% of BD_{CO2}, resulting in a significant decrease in free lime content. The aggregates were mainly in the $4 < x < 10$ mm granule size range, with the compressive strength being up to 4.5 MPa and the apparent density close to $2.1 g/cm^3$. Generally, compared to burnt oil shale alone, the mixtures of different wastes after addition of cement produced stronger granules. This indicates that better results could be achieved by the further optimisation of the mixtures. The BOS collected from the SO_2 removal system provided the weakest granules, which was attributed to its very slow hardening dynamics.

The granulation process under the accelerated carbonation conditions led to a significant decrease in the pH levels and electrical conductivity values of the leachate. In the case of hazardous MSWI APC residues, the mobility of chloride and heavy metals could be decreased by optimising the mixtures. The leaching test indicated that the granules suffered from some weight loss at current cement additions (5–10%). These granules shall be studied further to elucidate their potential to be used in the production of building blocks.

Finally, the results of this study could serve as the first step towards closing the waste cycle in Estonian energy and cement sectors, to achieve national targets of promoting waste recovery, reducing waste dumping and decreasing greenhouse gas emissions for a sustainable future.

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PAPER 3

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Original Article

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Accelerated carbonation technology granulation of industrial waste: Effects of mixture composition on product properties

Hakan Berber[1], Kadriann Tamm[2], Mari-Liis Leinus[2], Rein Kuusik[2], Kaia Tõnsuaadu[2], Peeter Paaver[3] and Mai Uibu[2]

Abstract

The use of accelerated carbonation technology in combination with a granulation process was employed to produce aggregates from a variety of industrial wastes, which included municipal solid waste incineration fly ash and air pollution control residue, oil shale ash, cement kiln dust, and quarry fines that have been produced in Estonia. Focusing mainly on the effects produced by the content of municipal solid waste incineration ash in the admixtures, the granule compositions were varied in order to tailor granule properties on the basis of CO_2 uptake, strength development, leaching behaviour, microstructure, and morphology. All the steps involved in the accelerated carbonation technology granulation process, from mixing with additives to granulation and carbonation treatment, were carried out in the same apparatus – an Eirich EL1 intensive mixer/granulator. The amount of CO_2 that was bound ranged from 23 to 108 kg per tonne of waste. The granules that included the optimised mixture of municipal solid waste incineration air pollution control residue, oil shale ash, cement kiln dust, and ordinary Portland cement were characterised by the highest compressive strength (4.03 MPa) and water durability for the size range of 4–10 mm. In addition, the process was found to be effective in reducing alkalinity ($pH < 11.5$) and immobilising heavy metals (especially zinc) and chloride. The composition and properties of the respective waste materials and mechanisms associated with the characteristics of the resulting granules were also addressed.

Keywords

Municipal solid waste incineration fly ashes, carbonation, granulation, oil shale ashes, compressive strength, microstructure, leaching, morphology

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Introduction

Ever-increasing world energy consumption levels have resulted in a significant rise in global CO_2 emissions, rising by 29.26% in 2017 when compared with the figures for 2000 (International Energy Agency, 2017). The use of fossil fuels accounted for more than 80% of global energy consumption in 2013, while it is anticipated to remain a primary energy source in 2040 (International Energy Agency, 2015). In addition, significant amounts of industrial by-products are generated from the use of fossil fuels.

In the Republic of Estonia, the primary energy source is calcareous kerogenous oil shale (OS), which is a low-grade solid fuel. In 2018, a total of 15.6 mt of OS was used in power and oil production, resulting in 11.3 mt of CO_2 emissions and the generation of 7.2 mt of alkaline OS ash (OSA). Only 1%–3% of OSA is currently utilised in construction materials or the agricultural industry, leaving about 7 mt to be deposited in the ash fields every year (Eesti Energia AS, 2018). Estonian OSA is classified as a hazardous waste according to EU Regulation 1357/2014, owing to its high free lime content causing high alkalinity (Environmental Investment Centre, 2019). In addition, since 2013, Estonia has been incinerating municipal solid waste (MSW) to produce heat and electricity. In Europe, energy recovery from MSW is managed primarily by MSW incineration (MSWI) technologies (Grammelis, 2011). The amount of MSW incinerated in the EU-27 rose by 99% between 1995 and 2015 (Eurostat, 2017). Although MSWI leads to a significant reduction in waste in terms of mass (up to 70%) and volume (up to 90%), it is still accompanied by the generation of fly

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ash (FA) from boilers, air pollution control (APC) residues and bottom ash (BA), which are the final sinks of several toxic heavy metals, as well as leachable chlorides, sulphates, and fluorides (Bobicki et al., 2012; Bodor et al., 2013; Costa et al., 2007; Fernández et al., 2004; Li et al., 2007; Wang et al., 2010). MSWI FA is classified as a hazardous waste under code 19 01 07 in the European Waste Catalogue (European Commission Decision, 2000) owing to its enriched heavy metal content and very fine particles. In 2017, the waste-to-energy (WtE) unit at the Iru Power Plant in Estonia incinerated approximately 235 kt of mixed MSW, resulting in 53 kt y^{-1} of BA, 3.7 kt y^{-1} of FA from the boiler, and 8.3 kt y^{-1} of APC residues (Enefit Renewable Energy, 2017). In Estonia, there is no current treatment technology for the MSWI ash from the Iru Power Plant, and it is currently transferred to a waste management company that has expertise in handling hazardous waste (Enefit Renewable Energy, 2016). The other major alkaline waste flow in Estonia is cement kiln dust (CKD). This is generated by AS Kunda Nordic Tsement, which produces constructional cements and crushed limestone. CKD is generally characterised by high alkalinity (pH $>$ 11.5) as well as high levels of copper, zinc, and lead (Gunning et al., 2010). Therefore, a solidification–stabilisation process is necessary for such alkaline and hazardous materials prior to their final disposal.

Mineral carbonation technology has the potential for stabilisation of alkaline wastes and long-term storage of atmospheric CO_2 (Bodor et al., 2013; Costa et al., 2007; Li et al., 2007; Seifritz, 1990). Since the potential for geological storage of CO_2 in Estonia is close to zero, mineral carbonation becomes a viable option for the safe storage of CO_2 (Shogenova, 2009). The high content of free lime (12%–25% free CaO, depending on fuel composition and combustion regimes) in Estonian OSA holds great potential for becoming a CO_2 sink for as much as 100–160 kg of CO_2 per tonne of Estonian OSA, which equals 1–1.2 mt annually (Uibu et al., 2009, 2011; Velts et al., 2011).

Several studies have focused on the stabilisation of MSWI ash through accelerated carbonation technology (ACT). The advantages of ACT can be stated as follows: (1) the residues show a significantly high reactivity towards CO_2, owing to the high content of lime and portlandite (Bogush et al., 2015; Huntzinger et al., 2009); (2) the alkalinity of the residues may be reduced (Astrup et al., 2006; Cappai et al., 2012; Gunning et al., 2010; Zhang et al., 2008); (3) the mobility of heavy metals such as lead, zinc, chromium, and copper is lowered (Baciocchi et al., 2009; Cappai et al., 2012). However, ACT may not reduce the leaching of chlorides, sulphates, or fluorides (Gunning et al., 2010).

ACT has been applied for the commercial production of aggregates from MSWI wastes. This process consist of several stages: The wastes and water are first mixed in a premixer, then conveyed into a pelletising drum, and finally into a curing chamber (Gunning et al., 2009).

This study aims to simplify the ACT granulation process by carrying out premixing, hydration, accelerated carbonation, and combined carbonation–granulation of wastes in the same apparatus. The main focus of the current study is to incorporate hazardous MSWI ash into mixtures of OSA, CKD, and quarry fines in order to produce granulated products that could be reused or declassified. The proportion of MSWI ash in the mixtures varied from 1% to 100% in order to elaborate its effect on CO_2 uptake as well as granule composition, microstructure, mechanical properties, and leaching characteristics. The application of this treatment process could assist in reducing the environmental impact of residues originating in Estonian power plants and the cement industry through the implementation of a circular economy and the abatement of CO_2 emissions, in line with the targets (i.e. reduction in hazardous waste disposal and climate change mitigation) that were set out by the Estonian Environmental Strategy 2030 (Estonian Ministry of Environment, 2007) and the European Environment Policy 2050 (European Commission, 2018).

Materials and methods

Initial materials

The two types of MSWI residues investigated in this study were collected from the WtE unit at the Iru MSWI power plant in Tallinn, Estonia. The MSWI FA was gathered directly from the boiler without any treatment process applied, and the MSWI APC residues were collected from a semi-dry APC unit at this plant. The APC system consists of a reactor and a baghouse filter, into which hydrated lime and activated carbon are injected in order to eliminate acid gases and organic pollutants. Solid residues were obtained both from the reactor and the baghouse filter, and were delivered to the residue silos in a mixed form.

The OSA sample was collected from the electrostatic precipitators (first field) at Auvere power plant in Estonia, where OS is burned in the circulating fluidised bed combustors (CFBCs).

The CKD, quarry fines, and ordinary Portland cement (OPC, CEM I, 42.5R) were obtained from AS Nordic Kunda Tsement in Estonia. All samples were received dry and homogenised and were subsequently stored at room temperature in airtight, sealed plastic containers.

Physical properties. The Brunauer, Emmett, and Teller (BET)-specific surface area (SSA) and particle size distribution (PSD) were determined using a Kelvin 1042 sorptometer and Horiba LA-950 laser-scattering PSD analyser, respectively.

The PSD and SSA values for the initial materials are given in Figure 1. The fine-grained materials (such as APC residues, OSA, OPC, CKD) tend to have an enhanced granulation characteristic owing to the fact that fine-grained materials have an increased particle contact, as well as possessing an improved binder dispersion (Barnard et al., 2005; Molenaar and Venmans, 1993). However, in very fine-grained materials, the reaction could be inhibited owing to tighter particle packing restricting CO_2 permeation (Johnson, 2000; Zhang et al., 2004). The PSD for CKD was characterised by a bimodal distribution, while that of MSWI FA, MSWI APC residues, OSA, and OPC was characterised by a normal distribution (Figure 1). MSWI FA that was collected directly from the boiler had notably coarser features than the other initial materials, except for the quarry fines. The grain size

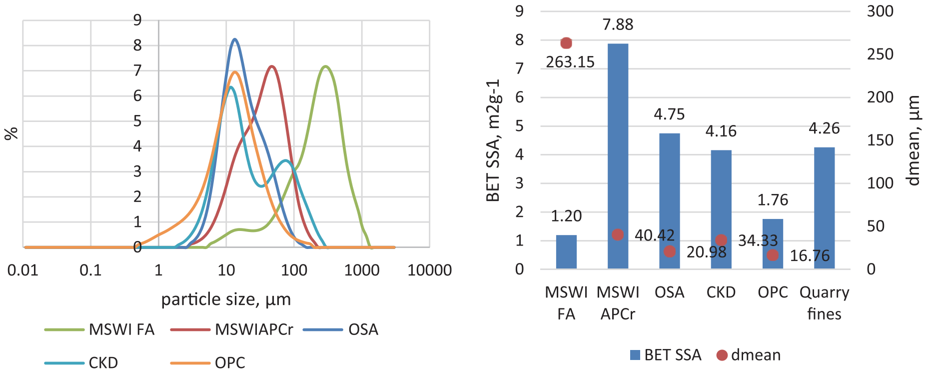

Figure 1. PSD and SSA of the initial materials.

Table 1. Chemical composition of initial materials.

	MSWI FA	MSWI APC residues	CKD	OSA	OPC	Quarry fines
fCaO, wt%	1.20	10.02	2.01	12	2.54	0.03
CO_2, wt%	3.58	6.35	20.30	5.31	1.80	41.12
Major elements, wt%						
Si	6.74	2.67	3.78	11.20	nd	nd
Al	3.94	0.86	1.88	5.81	nd	nd
Ti	1.38	0.40	0.11	0.31	nd	nd
Fe	2.37	0.63	1.41	3.74	nd	nd
Mn	0.12	0.05	0.06	0.03	nd	nd
Ca	22.87	21.30	22.67	26.62	nd	nd
Mg	1.20	0.90	0.48	1.46	nd	nd
Na	1.71	7.05	0.20	0.08	nd	nd
K	1.63	5.07	12.08	3.26	nd	nd
P	0.80	0.25	0.13	0.05	nd	nd
S	2.08	3.08	2.55	1.43	1.41	nd
Cl	3.34	24.11	5.35	0.46	nd	nd
Cr	0.095	0.046	0.005	0.006	nd	nd
Major heavy metals, ppm						
Ba	1425	410	187	208	nd	nd
Ni	174	77	62	67	nd	nd
Cu	417	712	43	45	nd	nd
Zn	3109	9745	812	88	nd	nd
Pb	280	2107	1894	131	nd	nd

MSWI: municipal solid waste incineration; FA: fly ash; APC: air pollution control; CKD: cement kiln dust; OSA: oil shale ash; OPC: ordinary Portland cement; nd: not determined.

composition of the coarse quarry fines was determined by sieving: $10 \geqslant d \geqslant 7\,\mathrm{mm} = 1.0\%$; $7 \geqslant d \geqslant 5\,\mathrm{mm} = 8.6\%$, $5 \geqslant d \geqslant 4\,\mathrm{mm} = 10.5\%$, $4 \geqslant d \geqslant 3\,\mathrm{mm} = 9.4\%$, $3 \geqslant d \geqslant 2\,\mathrm{mm} = 14.4\%$, $2 \geqslant d \geqslant 1\,\mathrm{mm} = 17.8\%$, $1 \geqslant d \geqslant 0.63\,\mathrm{mm} = 6.6\%$, $0.63 \geqslant d \geqslant 0.4\,\mathrm{mm} = 7.2\%$, $0.4 \geqslant d \geqslant 0.16\,\mathrm{mm} = 11.0\%$, $0.16 \geqslant d \geqslant 0.045\,\mathrm{mm} = 13.0\%$.

The other important physical property is SSA, since the carbonation reaction and granulation ability are promoted by the presence of a higher number of sites available in the initial material (Arandigoyen et al., 2006). The MSWI FA and OPC have lower SSA values compared with those of MSWI APC residues, OSA, and CKD. On average, the SSA values for MSWI ash deviate between 1.93 and 5.1 $\mathrm{m^2g^{-1}}$ (Lassesson et al., 2014; Liu et al., 2012; Ni et al., 2017).

Chemical and phase composition. The materials were characterised by using both X-ray fluorescence (XRF) spectroscopy (Rigaku Primus II) and quantitative X-ray diffraction (XRD) (Bruker D8 Advanced) methods (Table 1). A scanning step of $0.02^{o}\ 2\theta$ from 2^{o} to 75^{o} and counting time of 0.5 s were used. A quantitative mineral content of powdered material was measured using the Rietveld base code Siroquant-3.

The results of quantitative XRD analysis (Figure 2) show that OSA and MSWI APC residues include significant amounts of lime and portlandite, which are the main binders of CO_2. However, the amount of portlandite was negligible in the MSWI FA and CKD. Calcium-silicates could also play an important role in storing CO_2 (Johnson, 2000; Uibu et al., 2010, 2011).

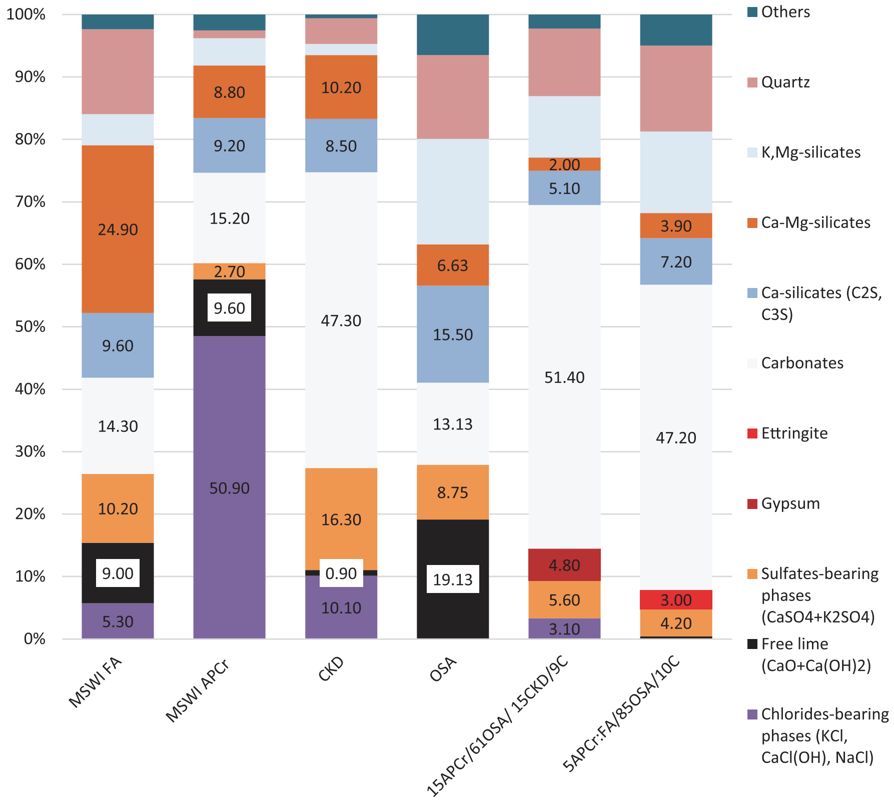

Figure 2. The phase composition of initial MSWI APC residues, CKD, and OSA, as well as granulated products.

Calcium-silicates, such as C2S and merwinite, were detected in the residues, at between 8.5%–12.4% and 1.8%–11.6%, respectively. High amounts of soluble salts (such as NaCl and KCl) and CaCl(OH), which were detected in APC residues, are the source of high contents of chlorine. The OPC sample was composed of alite, belite, aluminate, and gypsum, as the quarry fines contained mainly calcite.

Methods

Different mixtures were tested by ACT granulation in order to optimise the granule composition by varying the share of MSWI ash from 100% to 1%. The codes of the mixtures that were used to produce granules are given in Table 2 (Q stands for 30% of quarry fines and C stands for the portion of OPC).

Premixing, hydration, and carbonation (Step 1), followed by combined carbonation-granulation (Step 2), were all carried out in an Eirich GmbH and Co EL1-type intensive mixer/granulator by operating under different regimes. In Step 1, the rotational speed of the rotor tool was set at 3000 r min^{-1} for intensive mixing in a clockwise direction, while in Step 2 of combined carbonation–granulation it was set at 610 r min^{-1} in an anticlockwise motion. The mixing pan was operated at a slow speed (85 r min^{-1}) throughout the experiment. First, the initial materials (200 g) were mixed with water (L/S = 0.2–0.3 w/w) for 2 min. Then, a gas flow of 20% CO_2 in air was fed into the equipment at a rate of 100 L h^{-1} for 30 min. The main goal of the first carbonation step was to bind the fCaO of the initial materials into carbonates before the formation of granules would inhibit CO_2 diffusion into the core. This would help with: (1) maximising the amount of CO_2 to be bound into the granulated products; (2) improving the environmental properties of granulated products by reducing alkalinity and capsuling heavy metals; (3) improving the homogeneity of the granule. Additives, such as OPC and/or quarry fines, were added prior to Step 2. To begin the granulation process (Step 2), water was added as a liquid binder (L/S = 0.2–0.5 w/w) to initiate particle agglomeration. Once the desired granules had been formed, the gas flow of 20% CO_2 in air was led into the equipment for 20 min prior to collecting the granulated products. The main objective of the second carbonation step was to induce hardening of the granules by hydration and carbonation of cementitious materials (OPC, OSA, CKD, APC residues).

A portion of the granules (10 g) was dried in a thermostat for 2 h at 105°C, and was analysed for total carbon (TC) and free lime content. To determine the free lime (fCaO) content, which includes lime and portlandite, the analytical ethylene glycol method was employed (Reispere, 1966). The TC content was determined using an Electra CS-580 Carbon/Sulphur

Table 2. The compositions of the mixtures that were used to produce granules.

Mixtures	MSWI FA %	MSWI APC residues %	OSA %	CKD %	Quarry fines %	OPC %
100APCr	—	100	—	—	—	—
95APCr/5C	—	95	—	—	—	5
100OSA	—	—	100	—	—	—
65APCr:FA/Q/5C	24	41	—	—	30	5
60APCr:FA/Q/10C	22	38	—	—	30	10
1APCr:FA/94OSA/5C	0.37	0.63	94	—	—	5
1APCr:FA/89OSA/10C	0.37	0.63	89	—	—	10
1APCr:FA/64OSA/Q/5C	0.37	0.63	64	—	30	5
1APCr:FA/59OSA/Q/10C	0.37	0.63	59	—	30	10
5APCr:FA/90OSA/5C	1.85	3.15	90	—	—	5
5APCr:FA/85OSA/10C	1.85	3.15	85	—	—	10
5APCr:FA/60OSA/Q/5C	1.85	3.15	60	—	30	5
5APCr:FA/55OSA/Q/10C	1.85	3.15	55	—	30	10
15APCr/61OSA/15CKD/9C	—	15	61	15	—	9
11APCr/43OSA/15CKD/Q/5C	—	11	43	11	30	5

MSWI: municipal solid waste incineration; FA: fly ash; APC: air pollution control; OSA: oil shale ash; CKD: cement kiln dust; OPC: ordinary Portland cement.

determinator. The content of sulphates was determined in accordance with EVS 664:1995.

The carbon dioxide binding degree (BD_{CO2}), which is considered to be one of the main indicators of carbonation efficiency, was calculated using equation (1), where $CO_{2granules}$ is the analytically determined CO_2 content of the granules and CO_{2max} is the maximum possible CO_2 content of the granulated mixture of ash, OPC, and quarry fines in percentage according to equation (2). CO_{2max} is calculated on the basis of the phase contents of the mixture considering the mineralogy of each material, where $CaO_{free}{}^{i}$, $CaSiO_3{}^{i}$, $Ca_2SiO_4{}^{i}$, $Ca_3Mg(SiO_4)_2{}^{i}$, $Ca_3SiO_5{}^{i}$, $Ca_3Al_2O_6{}^{i}$, and $CO_2{}^{i}$ are the percentages of free lime, wollastonite, belite, merwinite, alite, Ca-aluminate, and mineral CO_2 in the initial materials:

$$BD_{CO_2} = \frac{CO_{2granules}}{CO_{2max}} \times 100,\% \tag{1}$$

$$CO_{2\max} = \frac{\frac{CaO^{i}_{free} \times M_{CO_2}}{M_{CaO}} + \frac{CaSiO^{i}_{3} \times M_{CO_2}}{M_{CaSiO_3}} + \frac{2Ca_2SiO^{i}_{4} \times M_{CO_2}}{M_{Ca_2SiO_4}} + \frac{3Ca_3Mg(SiO_4)^{i}_{4} \times M_{CO_2}}{M_{Ca_3Mg(SiO_4)_2}} + \frac{3Ca_3SiO^{i}_{5} \times M_{CO_2}}{M_{Ca_3SiO_5}} + \frac{3Ca_3Al_2O^{i}_{6} \times M_{CO_2}}{M_{Ca_3Al_2O_6}} + CO^{i}_{2}}{100 + \frac{CaO^{i}_{free} \times M_{CO_2}}{M_{CaO}} + \frac{CaSiO^{i}_{3} \times M_{CO_2}}{M_{CaSiO_3}} + \frac{2Ca_2SiO^{i}_{4} \times M_{CO_2}}{M_{Ca_2SiO_4}} + \frac{3Ca_3Mg(SiO_4)^{i}_{4} \times M_{CO_2}}{M_{Ca_3Mg(SiO_4)_2}} + \frac{3Ca_3SiO^{i}_{5} \times M_{CO_2}}{M_{Ca_3SiO_5}} + \frac{3Ca_3Al_2O^{i}_{6} \times M_{CO_2}}{M_{Ca_3Al_2O_6}} + CO^{i}_{2}} \times 100,\% \tag{2}$$

After 7 days of curing at room temperature, a sieve analysis was used to obtain the PSD of the granules, which was followed by a compressive strength analysis using the Brookfield CT3 25K texture analyser according to CEN-EN 1097-11:2013. At least ten granules were tested from each batch.

The apparent density (in accordance with EVS-EN 1097-6) of granulated products was determined after 7 days. A Mettler Toledo's density kit with universal basket for non-floating granules was used for the density determination process.

Leaching tests were carried out according to European standard EN 12457-2:2002. The ash or granules/deionised water (1/10) suspensions were kept in sealed centrifuge tubes for 24 h in an overhead shaker (GFL 3025) at 38 r min^{-1} (± 2) throughout the course of the experiment. The granules were not crushed prior the leaching test. The suspensions were filtered using a vacuum filter (Munktell filter paper, 100 g m^{-2}). The leachate pH was determined using a Mettler Toledo SevenGo pH, and electrical conductivity with a Mettler Toledo SevenGo Duo Pro. The composition of leachates was determined according to DIN EN ISO 10304-1/-2(D19/20, E29) by GBA Gesellschaft für Bioanalytik mbH. The content of Cl^- and SO_4^{2-} ions was determined using a Lovibond Spectro Direct

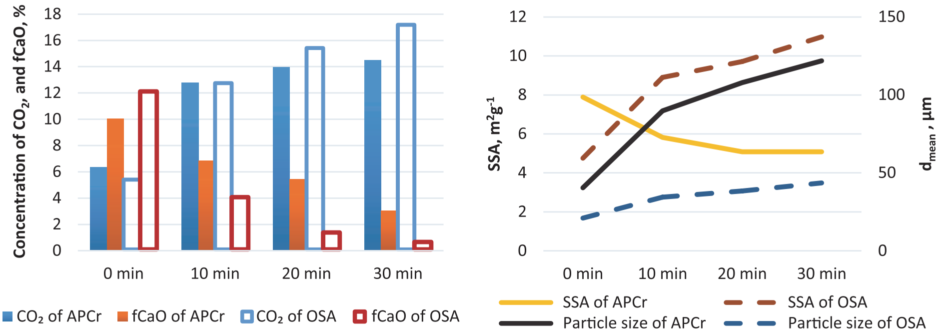

Figure 3. The changes in fCaO, mineral CO_2, mean particle size, and SSA of the initial APC residues and OSA during 30 min of carbonation.

spectrometer: Silver nitrate turbidity, and barium sulphate turbidity methods, respectively.

Fourier-transform infrared spectroscopy (FTIR) spectra were recorded with a diamond crystal Bruker 55/S/NIR FTIR ATR spectrometer, at an average of 24 scans, at a resolution of 4 cm^{-1}. The granules from the 5–7 mm batch were equally scrapped into three layers and milled prior to the FTIR analysis.

Microstructure observation and composition analysis were carried out using scanning electron microscopy and energy dispersive X-ray microanalysis methods (SEM-EDS), using a Zeiss EVO MA15 microscope with an INCA Energy 350 analyser. An accelerating voltage of 20 kV was used in the analysis. From every sample, six X-ray spectra were collected from different locations, and the results were averaged.

Pore size distribution and porosity of granules were determined by mercury intrusion porosimetry (MIP) using a POREMASTER-60-17 porosimeter (Quantachrome Instruments).

Results and discussions

CO_2 binding in the ACT granulation of waste

The CO_2 capture is mainly attributed to the relatively high contents of free lime in the initial samples. The CO_2 uptake is mainly attributed to the free lime content, which is relatively high (10%–15%) in OSA and MSWI APC residues samples, but negligible in CKD, MSWI FA, OPC, and quarry fines (Table 1). In Carbonation Step 1, the behaviour of OSA and MSWI APC residues in terms of CO_2 reactivity were investigated. The tests indicated that the fCaO content of OSA (12.03%) was exhausted (0.56%) within 30 min in Carbonation Step 1 under the conditions that included a low-range water-to-solid ratio (0.33 w/w) and a gas flow of 20% CO_2 in air. Carbonation of OSA led to a substantial increase (130%) in SSA and rather small increase in mean particle size (volume mean diameter d[4;3]), which indicates that agglomeration did not occur in Step 1 (Figure 3). The residual fCaO content remained at a higher level in carbonated APC residues. The substantial increase in mean particle size (201%) and decrease in SSA (35.6%) indicates that the agglomeration process had already started, which in turn inhibited CO_2 diffusion and the following carbonation reaction. In order to avoid agglomeration of APC residues, the water–solid ratio should be reduced. The effect of carbonation on the SSA of different materials also differs. Johannesson and Utgenannt (2001) and Uibu and Kuusik (2010) reported that the carbonation decreases the SSA of non-carbonated mortar owing to reaction products blocking the pores. Carbonation may increase the SSA of the material depending on the binder composition and water/binder ratio owing to microcracking as a result of the expansion of some products during the carbonation process (Arandigoyen et al., 2006). The results indicate that in order to achieve full carbonation of free lime, the agglomeration of waste particles in Carbonation Step 1 should be avoided.

However, the lack of free lime content after Carbonation Step 1 may be detrimental to the strength development of the granules in Step 2, since free lime acts as a potential binder by forming solid bridges in the granules. Therefore, the process parameters in Carbonation Step 1 will be studied further for each mixture, to optimise strength development and environmental properties.

The BD_{CO2} values of ACT granulated products were within the range of 50%–83%, indicating that the carbonation efficiency deviated from moderate to high, depending upon the mixture's composition (Tables 2–3). As expected, the granules that contained proportionally more MSWI ashes (100APCr, 95APCr/5C) tended to be less reactive towards CO_2 compared with the OSA-based granules, owing to early stage agglomeration (Figure 3, Table 4). Adding quarry fines and CKD as carbonates containing fillers into the mixture proportionally decreased the amount of CO_2 bound per tonne of waste (from 81–93 kg to 49–71 kg, Table 3).

In this study, the amount of CO_2 that was bound into granules ranged from 23 to 108 kg per tonne of waste. These results are in agreement with studies of similar waste types indicating that 8%–12% (w/w) of CO_2 could be trapped in the MSWI APC residues (Sun et al., 2008) and up to 29% (w/w) of CO_2 in the OSA (Sanna et al., 2014; Uibu et al., 2009). As the mixtures differed noticeably by the concentration of carbonatable content (free lime and

Table 3. CO_2 binding characteristics and mechanical properties of ACT granulated waste.

	Size distribution, %			Compressive strength, MPa	Apparent density, g/cm^3	BD_{CO2}, %	CO_2 bound, kg per waste t
Granules	7–10, mm	5–7, mm	4–5, mm	4–10, mm	4–10, mm	4–10, mm	4–10, mm
100APCr	58	34	1	2.88	1.75	56.49	45.62
95APCr/5C	17	50	22	3.93	1.96	49.87	39.71
100OSA	37	47	9	1.03	2.32	83.77	108.06
65APCr:FA/Q/5C	55	28	6	3.69	2.08	74.11	54.45
60APCr:FA/Q/10C	50	35	7	2.78	2.04	61.58	23.42
1APCr:FA/94OSA/5C	29	44	14	2.08	2.36	71.36	85.52
1APCr:FA/89OSA/10C	52	19	5	2.17	2.37	69.87	88.31
1APCr:FA/64OSA/Q/5C	25	48	13	1.91	2.52	82.93	67.78
1APCr:FA/59OSA/Q/10C	25	51	15	1.82	2.47	82.02	71.67
5APCr:FA/90OSA/5C	27	57	8	3.70	2.44	68.83	80.96
5APCr:FA/85OSA/10C	27	44	20	1.92	2.41	70.04	93.82
5APCr:FA/60OSA/Q/5C	36	38	13	2.07	2.50	81.91	65.71
5APCr:FA/55OSA/Q/10C	33	42	15	2.02	2.51	80.75	64.72
15APCr/61OSA/15CKD/9C	61	11	1	4.03	2.34	72.08	80.28
11APCr/43OSA/15CKD/Q/5C	67	20	3	3.06	2.42	79.79	49.08

Table 4. The release of components from initial and ACT granulated materials ('b' refers to the limit for landfilling of inert wastes, and 'c' to the landfilling limit for hazardous wastes) (Estonian Ministry of Environment, 2004).

Parameter	Limit (b)	Limit (c)	Unit	MSWI FA	MSWI APC residue	CKD	OSA	15APC/61OSA/ 15CKD/9C	11APC/43OSA/ 15CKD/Q/5C
pH	6-9		-	**13.9**	**13.3**	**13.9**	**13.5**	**11.7**	**11.6**
EC			mS cm^{-1}	17.5	61.3	39.3	12.6	12.4	10.10
TDS	4	100	g kg^{-1}	**87.9**	**306**	**196**	**63.1**	**685**	**505**
Chloride	0.8	25	g kg^{-1}	**16.8**	**192.2**	**40.8**	**2.1**	**30**	**24.4**
Fluoride	0.01	0.5	g kg^{-1}	**0.05**	<**0.15**	**0.26**	<**0.03**	<0.01	<0.01
Sulphate	1	50	g kg^{-1}	**10.8**	**14.6**	**53.2**	0.016	**8.9**	**8.25**
Ca			g kg^{-1}	15.1	73.7	26.6	10.9	7.5	6.5
K			g kg^{-1}	7.1	46.6	97.8	2.8	17.3	13.9
Na			g kg^{-1}	6.6	36.4	1.7	0.1	4.2	3.2
Mg			mg kg^{-1}	<1	<1	<1	2.4	1.3	1.2
Mn			mg kg^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hg	0.01	2	mg kg^{-1}	<0.002	**0.21**	<0.002	<0.002	<0.002	<0.002
Cd	0.04	5	mg kg^{-1}	0.009	<0.003	<0.003	<0.003	<0.003	<0.003
Pb	0.5	50	mg kg^{-1}	**4.7**	**700**	**22**	0.22	**36**	**28**
Cr	0.5	70	mg kg^{-1}	**17**	**2.6**	**4**	0.07	**3**	**2.4**
Ni	0.4	40	mg kg^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	4	200	mg kg^{-1}	**6.2**	**130**	0.5	0.09	<0.1	<0.1
Cu	2	100	mg kg^{-1}	0.2	**4.1**	<0.01	<0.01	0.05	<0.01
As	0.5	25	mg kg^{-1}	0.014	<0.005	0.015	<0.005	0.006	0.006
Mo	0.5	30	mg kg^{-1}	**1.8**	**4.5**	**2.5**	0.3	**2.1**	**1.9**
Ba	20	300	mg kg^{-1}	2.3	**29**	5.3	**27**	3.4	2.5

Note: Bold entries stand for the numbers higher than limit (b).
MSWI: municipal solid waste incineration; FA: fly ash; APC: air pollution control; CKD: cement kiln dust; OSA: oil shale ash; TDS: total dissolved solids.

calcium-silicates), the BD_{CO2} and the amount of CO_2 bound per tonne of waste were not directly dependent on each other.

Compositional changes and microstructure of ACT granulated wastes

The mineral compositions of two example granule batches are given in Figure 2. Following ACT, the carbonate content (as calcite and vaterite) increased in the result of carbonation of the free lime (lime and portlandite) and the other species (equation (2)). The phases of quartz, belite, merwinite, akermanite, and K-feldspar, which originated from OSA, MSWI ashes, CKD, and OPC, were also dominant in both batches of granules. The content of chlorides (halite, sylvite, and calcium hydroxyl chloride) positively correlated to the ratio of MSWI APC residues in the mixture. The phase compositions of the granules also revealed ettringite as a new formation, which may play a role in increasing the strength of the granules.

The FTIR analysis was conducted to support the results of the XRD analysis in terms of detection of carbonates and carbonatable contents, while observing the compositional changes in different layers of the granules (Figure 4). The broad absorption band at 3400 cm^{-1} represents the stretching vibrations of the O–H groups, while the band at 1622 cm^{-1} represents the bending vibrations of the O–H groups (Duan et al., 2013; Yousuf et al., 1993). In the initial materials, these bands were detected in the MSWI APC residues sample. These bands were rather stronger in the 95APCr/5C granules, which contained more unreacted portlandite, as well as CaCl(OH) and gypsum (Farmer, 1974; Siedl et al., 1969). These results confirm the low CO_2 binding degree of 95APCr/5C (49.87%) in comparison with OSA-based granules (Table 3). The broad absorption band at 1410 cm^{-1} represents the asymmetric stretching vibrations of the CO_3^{2-} ion, while the band at 875 cm^{-1} represents the bending vibrations of the CO_3^{2-} ion. The granules given in Figure 4(b)–(d) had somewhat stronger peaks at 1410 cm^{-1} compared with the initial materials (Figure 4(a)), which proves the formation of CO_3^{2-} by means of the carbonation process.

The wide range between 1200 cm^{-1} and 900 cm^{-1} is attributed to the symmetric and antisymmetric stretching of Si–O bonds. The main characteristic peaks of C–S–H correspond to the range between 1100 cm^{-1} and 900 cm^{-1}, since the compressive strength of the granules is partially governed by C–S–H (Hlobil et al., 2016; Puertas et al., 2012). The stronger Si–O bands correlate with the addition of cement. The broad band between 3600 cm^{-1} and 3100 cm^{-1} is assigned to the presence of ettringite, which resembles the broad OH band of H_2O in ettringite (Myneni et al., 1998). The presence of ettringite may have played a crucial role in generating high early strength (Duan et al., 2013; Uibu et al., 2016) in 95APCr/5C (3.93 MPa), in addition to the positive influence of C–S–H.

Comparing different layers of the granules regarding the content of OH$^-$, C=O and Si–O bonds indicated that the granules produced from 95APCr/5C and 15APCr/61OSA/15CKD/9C had a homogenous bond structure all around the granules (Figure 4(b) and (c)). However, the inner layer of batch 5APC:FA/85OSA/10C differed notably from the rest of the granule composition, which suggests possible boundary layers that could lead to cracking and loss of strength (Figure 4(d)). This indicates that too effective pre-carbonation may affect granule strength.

The scanning electron microscopy (SEM) photos reveal that the microstructure of the granules produced may have a significant impact on compressive strength values (Figure 5). For instance, the strongest granules (15APCr/61OSA/15CKD/9C) where characterised by dense, uniform, and stabilised matrices (Figure 5(a)). No cracks were detected. The SEM photos of 95APCr/5C revealed no boundary layers between the surface and the core (Figure 5(b)). The uniform structure could be one of the reasons for a relatively high compressive strength. The MIP analysis also suggests the lowest total intruded volume and smallest mean pore size among measured samples (Figure 6(a)). Decreasing the portion of MSWI ashes in the mixture from 95% to 1% led to an increase in the total intruded volume (0.0805 → 0.2261 cm^3 g^{-1}) as well as in mean pore size (Figure 6(a)). Larger pores can lead to cracks and voids.

Considering the fact that 5APCr:FA/85OSA/10C was characterised by the lowest compressive strength (Table 3), it was expected that many micro-cracks would be observed (Figure 5(c)). The SEM photo that was provided after the 24 h leaching test (Figure 5(d)) indicated that the magnitude of the cracks was substantially decreased or had disappeared entirely, and the compressive strength of the leached granules (5APCr:FA/85OSA/10C) had increased to 4.74 MPa. Similar tendencies were shown at an OSA-based stone formation by Uibu et al. (2016). The MIP analysis also revealed a decrease in the total intruded volume (0.2142 → 0.1865 cm^3 g^{-1}) as well as in mean pore size (Figure 6(b)).

The inclusion of quarry fines (30%) decreased the total intruded volume (0.2142 → 0.1610 cm^3 g^{-1} in the case of 5APC:FA/55OSA/Q/10C and 0.1587 → 0.1090 cm^3 g^{-1} in the case of 11APC/43OSA/15CKD/Q/5C), but increased the average pore size (Figure 6(c)). The latter indicates that the inclusion of quarry fines would probably increase the apparent density of the granules, but not the compressive strength values.

Mechanical properties of ACT granulated wastes

The granules produced were characterised by a size range of 4–10 mm (Table 3), possessing a regular shape (Figure 7), and compressive strength of 1.03–4.03 MPa, depending on the composition of the mixtures. Incorporation of MSWI ashes 5%–100% and cement 5%–10% enhanced the compressive strength of the granules. The mixtures that contained up to 15% APC residues, such as 15APCr/61OSA/15CKD/9C, resulted in the strongest and soundest granules, confirming the results shown by Berber et al. (2019). The granules that contained mainly OSA (100OSA, 1APCr:FA/94OSA/5C) remained noticeably weaker, and the partial replacement of the cementitious wastes with inert and coarse quarry fines (1APCr:FA/64OSA/Q/5C, 1APCr:FA/59OSA/Q/10C) decreased the compressive strength further (Table 3). This behaviour could be explained by considering the absence of CaO, which may act as a potential binder by forming solid bridges in the granules since the carbonatable content of quarry fines was negligible. In the case of OSA, the free lime was already exhausted prior to granulation and the second carbonation step (Figure 3). Previous studies have shown that the hydrous transformations of free lime, anhydrite, calcium-silicates, and amorphous Al-Si glass phases control the solidification of OSA via the formation of calcium-rich hydrate phases ($3CaO{\cdot}2SiO_2{\cdot}3H_2O$, $CaO{\cdot}SiO_2{\cdot}2H_2O$, $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) and by the carbonation of portlandite (Liira et al., 2009; Pihu et al., 2012; Uibu et al., 2016). The latter indicates that the first carbonation step requires further optimisation in order to support the strength development in the following stages.

Several studies have reported that the addition of a binder (such as OPC) increases the compressive strength of the aggregates (Colangelo et al., 2015; Gomathi and Sivakumar, 2012; Tang and Brouwers, 2017). For instance, Tang and Brouwers

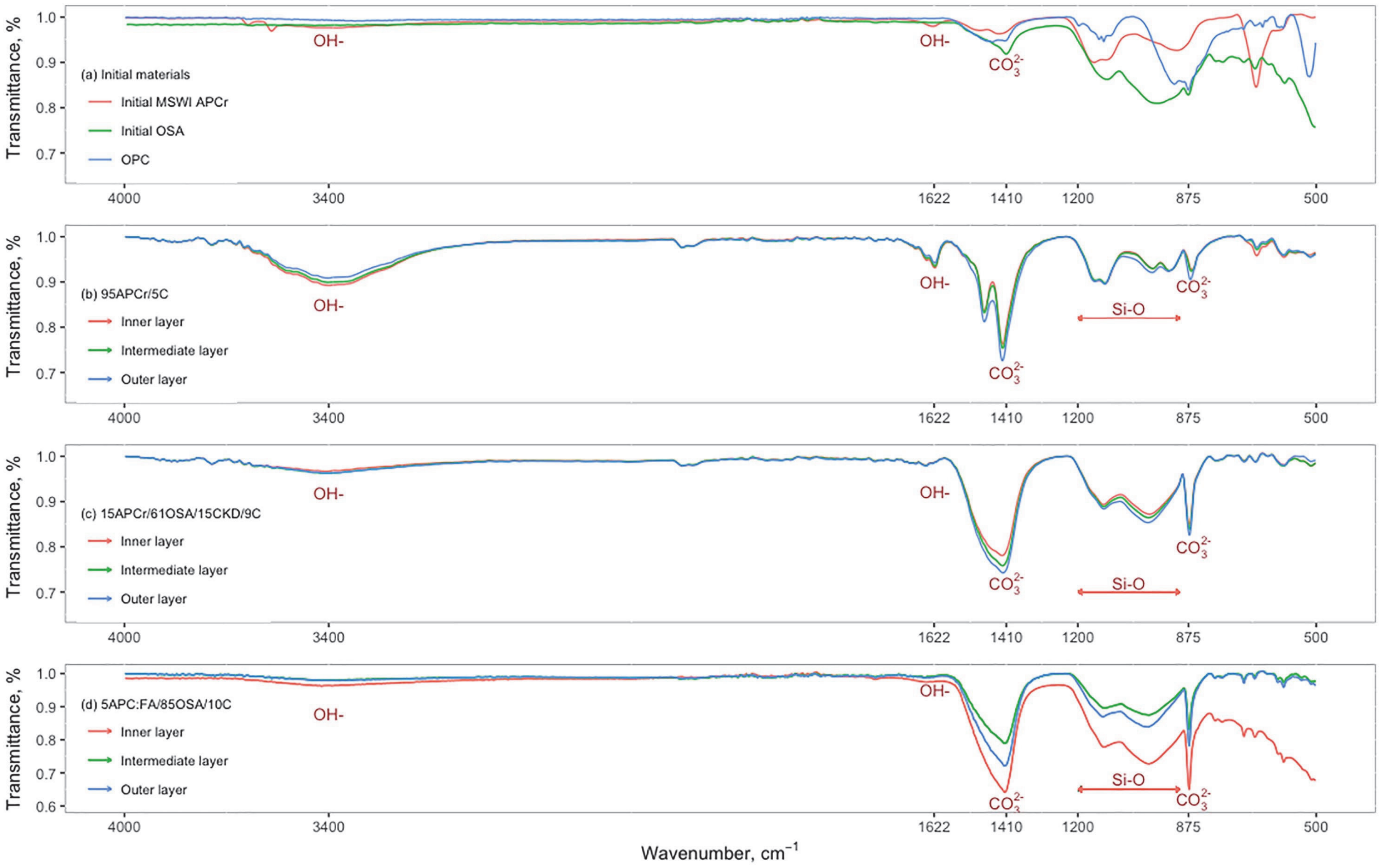

Figure 4. FTIR analysis of ACT granulated materials, focusing on the composition of different layers.

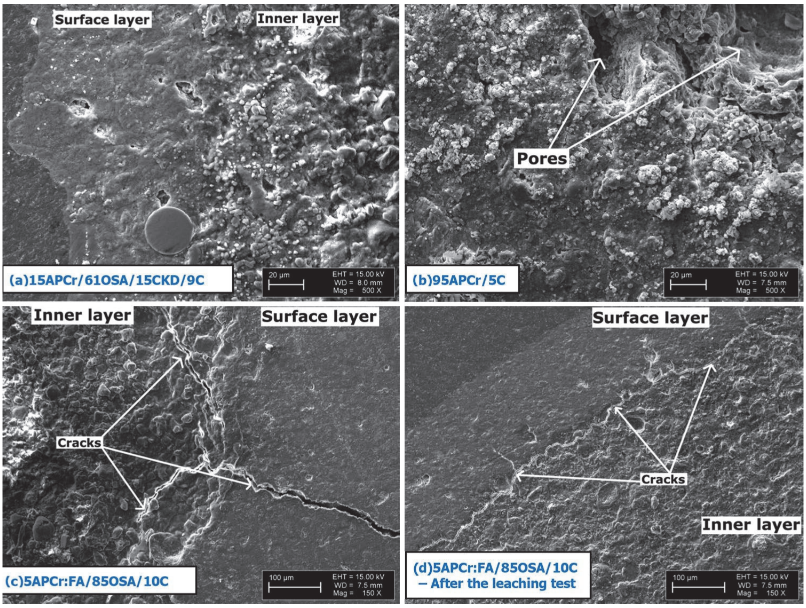

Figure 5. SEM graphs of the granules produced.

(2017) concluded that the incorporation of 10% and 15% OPC into MSWI BA fines produced a higher compressive strength when compared with a 5% OPC addition, by 14.7% and 22.5%, respectively. The factors that may have an adverse effect on compressive strength may be: Cracks owing to autogenous shrinkage (Afzal et al., 2014); cracks resulting from excessive heat in hydration (Chu et al., 2013); cracks owing to hydraulic shrinkage (Afzal et al., 2014); cracks owing to amorphous silica content (Joseph et al., 2018); and micro-cracks caused by a high water absorption rate (Lo et al., 1999). In this study, the inclusion of 5% OPC significantly increased the compressive strength of the granules, as the inclusion of 9%–10% OPC led to inconsistent results (Table 3). The latter indicates that in addition to mixture composition, the effect of processing conditions must be considered. The fact that the granules containing free lime were found to be stronger, and exposure to water (leaching test) promoted strength development, indicates that the first carbonation step and the curing step must be optimised further in order to guarantee a sufficient quantity of portlandite and alkaline reactive water inside the granules to form cementitious hydrates and $CaCO_3$ bridges that enhance strength. However, this may have a negative effect on CO_2 uptake.

The granules' apparent densities varied between 1.75 $g\,cm^{-3}$ (100APCr) and 2.52 $g\,cm^{-3}$ (1APCr:FA/64OSA/Q/5C), indicating that higher APC residues incorporation led to lower densities. This confirms the results of MIP measurements.

Leaching characteristics of ACT granulated wastes

Figure 8 and Table 4 show the results of the leaching tests that were carried out on the size fraction of 4–10 mm of granules containing 1%–100% of MSWI ash. The limit value 'b' refers to the limit landfilling of inert wastes and 'c' to the limit for the landfilling of hazardous wastes (Estonian Ministry of Environment, 2004) for the leaching of pH, chlorides, sulphates, and corresponding heavy metals that are referred to in the Estonian regulation for waste disposal.

In the case of the granules that contained >11% of MSWI ash, the pH values were higher than the limit (11.5) (Figure 8). These batches also suffered significant mass loss during the leaching test, which were also expressed by increased electrical conductivity (EC) values (Figure 8). One of the problematic parameters when it comes to the utilisation of MSWI APC residues is the leaching of chloride. As expected, chloride leaching was considerably higher than the limit of 25 $g\,kg^{-1}$ in the case of the granules, which contained >15% of MSWI ash. Increasing the content of OPC enhanced water durability as well as the further immobilisation of chloride, sulphate, zinc and EC (Figure 8, Table 4). The release of priority contaminants – mercury, cadmium, and nickel (Directive 2013/39/EU, 2013) – was below the detection limits at the given conditions in the case of ACT granulated 15APC/61OSA/15CKD/9C and 11APC/43OSA/15CKD/Q/5C (Table 4). The release of lead exceeded the limit for inert wastes. Among the hazardous elements arsenic, barium, chromium, molybdenum, and copper, according to national legislation, the release of chromium and molybdenum exceeded the limit for inert wastes. Partially substituting hazardous MSWI ash with quarry fines and/or OSA also improved the environmental characteristics of the resulting granules (Figure 8). Exposure to water promoted strength development and the recovery of cracks by completing the delayed reactions that were inhibited by the lack of water (Figures 5 and 6(b)).

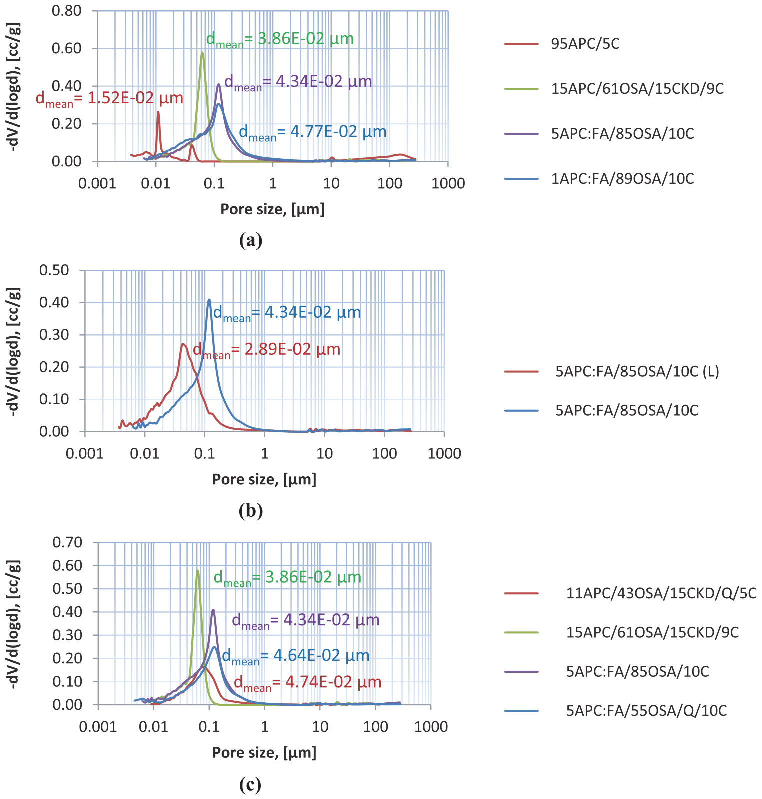

Figure 6. Pore size distribution of the granules produced.

Figure 7. Examples of ACT granulated wastes (5–7 mm).

The latter indicates that dense structure and relatively high compressive strength do not guarantee water durability if the granules contain highly leachable chloride compounds. In order to produce environmentally safe construction materials, the hazardous MSWI wastes should be combined with environmentally benign or less hazardous industrial by-products, such as quarry fines and OSA.

Conclusions

The ACT granulation was carried out on mixtures of different types of wastes in order to elaborate the effect of each of those on CO_2 uptake as well as granule composition, microstructure, mechanical properties, and leaching characteristics. The ACT granulation process was simplified by carrying out premixing, hydration, accelerated carbonation, and combined carbonation–granulation of wastes in the same apparatus. The main objective was to incorporate hazardous MSWI ash into mixtures of OSA, CKD, and quarry fines in order to produce sustainable construction aggregates. The tests performed with a high percentage of MSWI ash were undertaken in order to understand the influence of varying the mixture composition (i.e. mineralogy and reactivity during pre-carbonation).

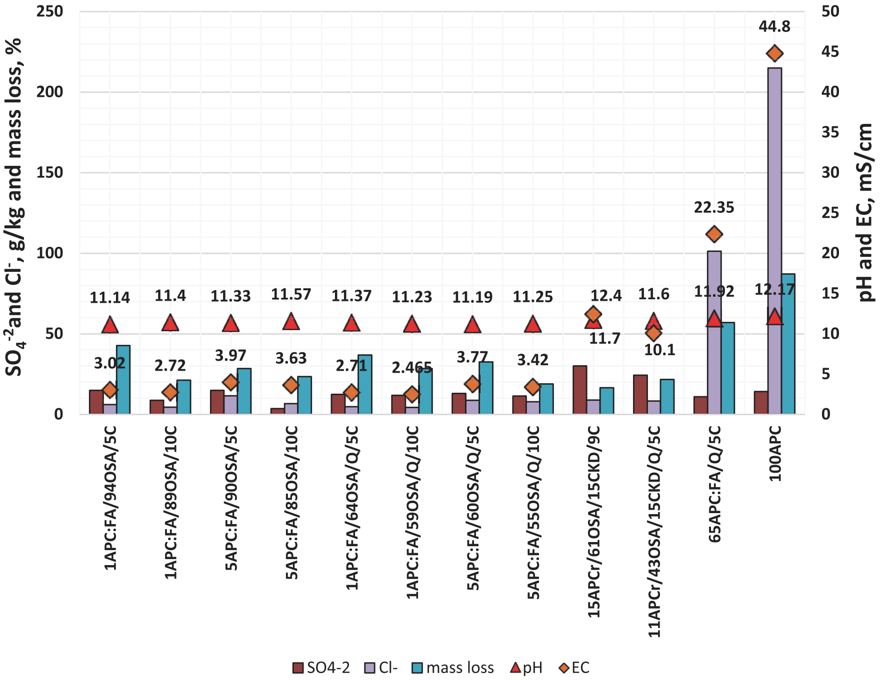

Figure 8. Mass loss, leachable sulphate and chloride ions (g kg^{-1}), and leachate pH and EC (mS cm^{-1}) values in ACT granulated waste (4–10 mm)

The CO_2 binding ability of waste depends primarily upon the content of fCaO and calcium-bearing silicates. The amount of CO_2 that was bound ranged between 23 and 108 kg per tonne of waste. The APC residues-based granules (60%–100% APC residues) tended to be less reactive towards ACT when compared with OSA-based granules (0%–15% APC residues) owing to early stage agglomeration.

However, those granules (APC residues-based) containing unreacted free lime were found to be stronger (2.8–3.9 MPa) than the OSA-based granules (1.0–2.2 MPa), because the higher pH of the pore solution increases the solubility of silica, which in turn forms cementitious hydrates, and the carbonation of portlandite forms $CaCO_3$ bridges between the particles that also enhance strength. Furthermore, contact with water promoted strength development because the delayed pozzolanic reactions may have been inhibited owing to lack of reactive water inside the granules. This indicates that the carbonation step before granulation, as well as the curing conditions after granulation, must be optimised further to enhance the strength development of granules.

The MIP and SEM analysis confirmed that compressive strength does not only depend upon the content of strength-giving phases (the added OPC), but also on the physical structure and microstructure. The dense and uniform structure resulted in a higher compressive strength, as the weakest granules were characterised by visible intersections between layers, pores, and cracks.

Adding OPC did not result in a proportional increase in compressive strength, but the inclusion of it enhanced water-durability and the further immobilisation of chloride, sulphate, and EC by more than 5%. The APC residues-based granules tended to decompose in water, and the leaching of chloride was well over the limit of 25 g kg^{-1}. The latter indicates that dense structure and relatively high compressive strength do not guarantee water-durability if the granules contain highly leachable chloride compounds. In order to produce environmentally safe construction materials, the hazardous MSWI wastes should be combined with environmentally benign or less hazardous industrial by-products, such as quarry fines and OSA. Those granules that included the mixture of MSWI APC residues, OSA, CKD, and 5%–9% OPC were characterised by the highest compressive strength (4.03 MPa) and water-durability for the size range of 4–10 mm. Additionally, the ACT granulation significantly reduced the mobility of zinc.

The results of this study provide a way of utilising wastes from the MSWI, power, and cement sectors. Subsequent studies will concentrate on further optimisation of ACT granulation operating conditions and incorporation of granulated products into building block production.

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Curriculum vitae

Personal data

Name: Hakan Berber
Date of birth: 06.11.1989
Place of birth: Isparta/Turkey
Citizenship: Turkish

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Education

Time Period	Educational Institution	Education (field of study/degree)
2015 –	Tallinn University of Technology	PhD in Environmental Engineering
2013 – 2015	Tallinn University of Technology	MSc in Environmental Engineering
2008 – 2012	Yildiz Technical University	BSc in Engineering
2003 – 2007	Isparta Anadolu High School	High school education

Language competence

Language	Level
Turkish	Native
English	Fluent
Estonian	Intermediate
Russian	Beginner

Professional employment

Time Period	Position	Organization
2017 –	Business Development Specialist	Department of Economics and Finance, Tallinn University of Technology
2017 –	Lecturer	Department of Economics and Finance, Tallinn University of Technology
2017 – 2017	Analyst	Foresight Centre – Parliament of Estonia
2014 – 2017	Trading Analyst	Genius Sports Services Eesti OÜ

Defended Thesis

- *MSc thesis:* Preliminary feasibility study of MSWI fly ash utilisation. Tallinn University of Technology, 2015. Supervised by Viktoria Voronova.

Main areas of scientific work

- Field of research: 1. Biosciences and Environment; 1.8. Research relating to the State of the Environment and to Environmental Protection; CERCS classification: T270 Environmental technology, pollution control
- Field of research: 4. Natural Sciences and Engineering; 4.11. Chemistry and Chemical Technology; CERCS classification: P360 Anorganic chemistry

Research projects

- VERT19042 – The Economic and Legal Evaluation of Digital Ecosystems in the EU (1.09.2019−31.08.2022). Funded by European Commission.
- LEP19010ME (RITA1/02-20-04) - Climate change mitigation with CCS and CCU technologies (1.04.2019−31.03.2021). Funded by Estonian Research Council.
- IUT33-19 – Fundamentals of multicomponent mineral-organic systems: Chemistry, modelling and sustainable processing (1.01.2015−31.12.2020). Funded by Estonian Research Council.
- KIK17083 – Production of construction materials from industrial wastes and CO_2 (21.12.2016−1.06.2018). Funded by Environmental Investment Centre.

Supervised dissertations

- Hareesh Gaddam, Master's Degree, 2018, (sup) Viktoria Voronova; Hakan Berber, Preliminary feasibility study of carbon capture and storage (CCS) technology in Estoniana Power Plants, Tallinn University of Technology.
- Erika-Henriet Aus, Master's Degree, 2016, (sup) Viktoria Voronova; Hakan Berber, Assessment of possibilities of hazardous waste utilisation in AS Norma, Tallinn University of Technology.

Accomplishments

- 2019 – Speaker in a panel discussion "Europe: Facing the Digital Challenge", Jean Monnet 30th Conference, European Commission.
- 2019 – Certificate of Appreciation for Marketing activities, Tallinn University of Technology
- 2018 – Smart Specialisation Scholarship, Archimedes Foundation.
- 2015 – PhD Scholarship, Tallinn University of Technology.
- 2015 – Cum laude graduate in Master's Studies, Tallinn University of Technology
- 2008 – Ranked in 1% out of 1.5 million candidates in natural sciences and mathematics, University Entrance Exam in Turkey (OSS).

Elulookirjeldus

Isikuandmed

Nimi: Hakan Berber
Sünniaeg: 06.11.1989
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Kodakondsus: Turkish

Kontaktandmed

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Hariduskäik

Töötamise aeg	Õppeasutus	Haridus (eriala/kraad)
2015 –	Tallinna Tehnikaülikool	Keskkonnatehnika doktorikraad
2013 – 2015	Tallinna Tehnikaülikool	Keskkonnatehnika magistrikraad
2008 – 2012	Yildizi Tehnikaülikool	Tehnikateaduste bakalaureus
2003 – 2007	Isparta Anadolu Keskkool	Keskkooli haridus

Keelteoskus

Keel	Tase
Türgi keel	Emakeel
Inglise keel	Kõrgtase
Eesti keel	Kesktase
Vene keel	Algtase

Teenistuskäik

Töötamise aeg	Ametikoht	Tööandja nimetus
2017 –	Ettevõtluse spetsialist	Majandusanalüüsi ja rahanduse instituut, Tallinna Tehnikaülikool
2017 –	Lektor	Majandusanalüüsi ja rahanduse instituut, Tallinna Tehnikaülikool
2017 – 2017	Analüütik	Arenguseire Keskus, Riigikogu
2014 – 2017	Kaubandusanalüütik	Genius Sports Services Eesti OÜ

Kaitstud lõputööd

- *Keskkonnatehnika magistrikraad:* Olmejäätmete põletamise lendtuha kasutamise eeluuring. Tallinna Tehnikaülikool, 2015. Juhendaja: Viktoria Voronova.

Teadustöö põhisuunad

- ETIS KLASSIFIKAATOR: 1. Bio- ja keskkonnateadused; 1.8. Keskkonnaseisundit ja keskkonnakaitset hõlmavad uuringud; CERCS KLASSIFIKAATOR: T270 Keskkonnatehnoloogia, reostuskontroll.
- ETIS KLASSIFIKAATOR: 4. Loodusteadused ja tehnika; 4.11. Keemia ja keemiatehnika; CERCS KLASSIFIKAATOR: P360 Anorgaaniline keemia.

Uurimisprojektid

- VERT19042 – Euroopa Liidu digitaalsete ökosüsteemide hindamine majanduslikest ja õiguslikest aspektidest. (1.09.2019−31.08.2022). Euroopa Komisjoni programm.
- LEP19010ME (RITA1/02-20-04) – Kliimamuutuste leevendamine läbi CCS ja CCU tehnoloogiate (1.04.2019−31.03.2021). Eesti Teadusagentuur.
- IUT33-19 – Multikomponentsete mineraal-orgaaniliste süsteemide käitlemise alused: keemia, modelleerimine ja kestlik kasutus (1.01.2015−31.12.2020). Eesti Teadusagentuur.
- KIK17083 – Uuring tööstusjäätmetest ehituslike täitematerjalide saamiseks koos CO2 sidumisega (21.12.2016−1.06.2018). Keskkonnainvesteeringute Keskus.

Supervised dissertations

- Hareesh Gaddam, Magistritöö, 2018. Süsiniku kogumise tehnoloogia teostatavusuuring Eesti Elektrijaamade näitel, Juhendajad: Viktoria Voronova, Hakan Berber. Tallinna Tehnikaülikool.
- Erika-Henriet Aus, Magistritöö, 2016. Assessment of possibilities of hazardous waste utilisation in AS Norma. Juhendajad: Viktoria Voronova, Hakan Berber. Tallinna Tehnikaülikool.

Saavutused

- 2019 – Kõneleja Euroopa Komisjoni Jean Monnet' meetmete 30. aastapäeva konverentsil vestlusringis teemal: "Euroopa - silmitsi digitaalse väljakutsega".
- 2019 – Tunnustus turundus tegevusalal, Tallinna Tehnikaülikool.
- 2019 – "Kõrghariduse erialastipendium nutika spetsialiseerumise kasvuvaldkondades", SA Archimedes.
- 2015 – Doktorantuuri stipendiaat, Tallinna Tehnikaülikool.
- 2015 – Keskonnatehnika magistrikraadi cum laude, Tallinna Tehnikaülikool.
- 2008 – Loodusteaduste ja matemaatika valdkonnas esimese 1% hulgas 1.5 miljoni kandidaadi seast Türgi ülikooli sisseastumiseksamitel (OSS).