Production of snow and ice melting agents - calcium and magnesium acetates from oil shale industry combustion waste

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Highlights

- Neutralization reaction between oil shale ash and acetic acid can give more than 90% yield of CMAs.
- As Ca and Mg are mainly in their oxide forms so the main by-product is water instead of CO_2.
- This method could be used on long term deposited oil shale ash in Estonia.

1. Introduction

In Estonia about 5 mln tons of oil shale ash is produced and only 2% of it is reused [1]. Previous research has determined that Estonian oil shale ashes chemical and mineral composition is rich in Ca where Ca compounds are mainly present as quicklime (CaO) or as slaked lime ($Ca(OH)_2$) [2],[3]. The high content of Ca and Mg in oil shale ashes makes it an attractive material for the production of environmentally friendly ice and snow repellant agents without emitting CO_2 into the environment. Currently Ca and Mg acetates are produced by mixing an equimolar amount of acetic acid into limestone or dolomite [4]. The disadvantage of using those carbon minerals is the emission of CO_2 into the atmosphere and the high cost of resource to mine and grind pure limestone. Using oil shale ash as the raw material for the production of snow repellant agents has many advantages: there is no need to mine it as it is directly available; the content of carbonate mineral is low therefore reacting with an acid the main by-product is water; low cost. From previous research it is known that in order to produce Ca and Mg formates from oil shale ash a wide range of formic acid solutions (20-100 %) can be used and 100 °C at normal pressure is enough [5]. In this work various organic acids and different reaction environments were used.

2. Methods

The oil shale ashes used in this work were provided by the Department of Energy Technology in Tallinn University of Technology. Three types of ashes were used in this work: cyclon, bottom and electric filter ash. The composition of oil shale ashes were determined by XRF and the main components are listed in Table 1. The XRF results show that the oil shale ash consists of high percentage of Ca and a relatively high content of Mg which can be used in order to produce their respective acetate salts.

Table 1. XRF results of Estonian oil shale ashes, wt%. PC – pulverized combustion, CFBC - Circulating Fluidized Bed Combustion

Ash	Power plant type	CaO	SiO_2	MgO	Al_2O_3	SO_3	Fe_2O_3	K_2O
Superheater fly ash	PC	48.79	24.82	6.12	6.65	4.83	3.78	2.29
Electric filter fly ash	CFBC	38.92	26.58	5.07	8.95	5.58	4.06	3.99
Bottom ash	CFBC	55.90	7.76	7.36	2.47	7.85	2.82	0.909

The set-up for the production of Ca and Mg acetates is shown in Figure 1. As these acetate salts are water soluble the yield of reactions was determined by measuring the Ca and Mg content in the filtrate at the Laboratory of Inorganic materials at Tallinn University of Technology using Atomic absorption Spectroscopy (Varian SpectrAA 50/55).

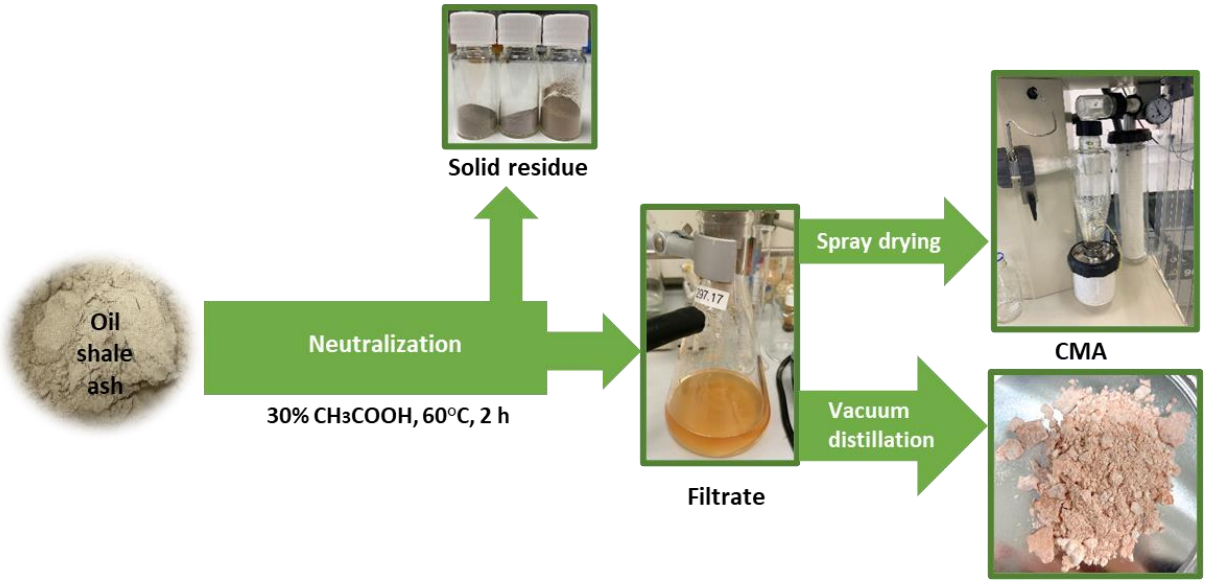

Figure 1. CMA production from oil shale ash.

3. Results and discussion

From the three types of oil shale ashes used the highest yield of Ca and Mg acetates (over 90%) was acquired with the PC superheater fly ash with 5 equivalents of acetic acid.

4. Conclusions

Using oil shale ashes from the oil shale industry as a source of ice melting agents by acetic acid neutralization reaction is a promising method to utilize the waste product. Furthermore as there already are deposits of oil shale ash in Estonia those deposits could be used and valorized.

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Keywords
Environmentally friendly ice melting agents, calcium magnesium acetates, oil shale ash, neutralization.