Oil shale ash based backfilling concrete – Strength development, mineral transformations and leachability

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HIGHLIGHTS

- Utilization of combustion and mining wastes to maximize oil shale recovery.
- Formation, environmental hazards and durability of ash-based backfilling concretes.
- Hardening and leaching dynamics in correlation with the ash stone mineralogy.

ARTICLE INFO

ABSTRACT

The combustion of oil shale (OS) in electric power plants is accompanied by the generation of vast amounts of waste ash. One promising idea to maximize the recovery of oil shale from mines is to backfill them with oil shale ash (OSA)-based concrete. However, the properties of this concrete have yet to be analyzed in detail and this approach also raises concerns about the risk of polluting both surface and groundwater. To address these concerns we developed different types of OSA-based concretes and characterized their structure and leaching characteristics. This information enables us to predict the type and durability of each respective ash stone. A compressive strength of 1–5 MPa was achieved after 7 days (maximum after 28 days > 25 MPa). During the early stages of curing, the pH and electrical conductivity (EC) of the leachates exceeded or were close to the limits set for general wastes, however, both properties decreased considerably after 28 days (pH < 11.5; EC < 1000 µs/cm). In order to utilize OSA on a large scale, the composite blends we developed should be further optimized by adding ground high-calcium fly ashes, Portland cement, or other components.

1. Introduction

Extensive use of low-grade solid fuels such as oil shale and brown coal for both power and oil production leads to a sizable solid waste stream. Estonian kukersite OS is the largest industrially exploitable OS resource in the world [1,2]. About 60% of Estonia's fuel balance is covered by OS (with an annual mining output of 14–16 Mt). Its share in power production exceeds 95% [1,3]. The main reason for this large-scale use of oil shale in Estonia is to ensure energetic security. On the other hand, both the extraction and use of OS is accompanied by negative environmental effects [4]. OS extraction and enrichment processes in Estonia result in

an annual formation of 4.5 Mt of waste rock material (the OS seam consists of up to 50% of limestone layers and concretions [5]) that is mostly deposited in the open spoil dumps [4,6]. Electricity generation using circulating fluidized bed combustion (CFB) or pulverized firing (PF), produces an additional waste ash stream of between 5 and 7 Mt annually. Despite of numerous studies in the field of waste rock material and OSA recycling; only ∼22% of the waste rock material is recycled as aggregate and a little more than 2% of OSA is used in the construction material industry or in agriculture [4]. Estonian strategic documents [7] envision recycling 50% of the waste rock material and more than 5% of OSA by 2030. The losses of OS in mining should not exceed 30% by the year 2030 [7]. The recovery of this mineral resource could be increased by backfilling OS mines. Preliminary calculations have shown that the load on a pillar does not exceed 4 MPa at an excavation depth
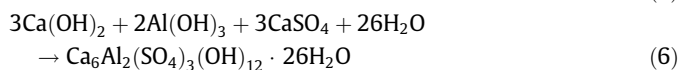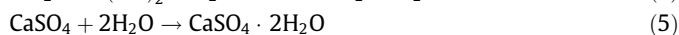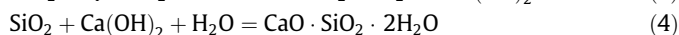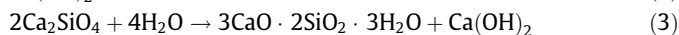
of 60–80 m when 50–80 vol-% of the space is backfilled [8]. Although the properties of OSA include resistance to freezing and thawing, OS waste rock can be utilized as aggregate in backfilling concrete under constant temperature conditions such as within underground OS mines, which remain between 6 and 8 °C [9].

Increasing the use of supplementary cementitious materials, such as fly ashes, silica fume, and steel slag within concrete is an obvious and necessary step to reduce both industrial waste streams and carbon emissions. These waste materials possess hydraulic and/or pozzolanic properties, and, when used in optimal levels, enhance the mechanical performance and durability of the concrete [10]. However, concretes that contain these supplementary cementitious materials tend to have slower strength development because the hydraulic Portland cement reaction is much faster than the pozzolanic reaction [10]. Although recent trends clearly support the use of supplementary cementitious materials in concrete, their widespread use is limited by other factors, including the replacement percentage which is typically between 20% and 50% [10], and lack of suitable applications. One way of using either waste incinerator or power-plant ashes is to use this ash as a controlled low-strength material [11]. Controlled low-strength material has been defined as a material that has a compressive strength of 8.3 MPa or less; is self-compacting, flowable, and used primarily as a replacement for soil and structural filling applications such as pipeline bedding, tilt-up construction, foundation backfill, filling abandoned mines and the space under slab voids, and sequential excavations in contaminated soils [12].

A number of previous OSA studies [1,13,14] have shown that the hydrous transformation of free lime (CaO), anhydrite (CaSO$_4$), secondary Ca(Mg)-silicate minerals and amorphous Al–Si glass phases control the solidification/cementation of OSA mainly via the formation of secondary Ca-rich hydrate phases and by the carbonation of portlandite. OSA hydration and hardening for the purpose of composite formation involves slaking the lime to form portlandite (Eq. (1)), which reacts with the CO$_2$ in air to form calcite (Eq. (2)). Secondary silicates, such as larnite are converted into 3CaO·2SiO$_2$·3H$_2$O and portlandite by hydration (Eq. (3)). These silica or silicates can, in turn, react with Ca(OH)$_2$ (Eq. (4)). OSA hydration also involves anhydrite conversion to gypsum and the formation of ettringite (Eqs. (5) and (6)) [1]. Ettringite is a primary phase that is reported to form during the hydration of alkaline ash, which also captures a number of trace elements [15,16]. Ettringite is stable in the presence of excess CaSO$_4$ and solid Ca(OH)$_2$ at pH levels between 10.7 and 13.0 [16]. Soluble sulfates can be the limiting factor during transformation, especially in the case of PF ashes, and the transformation proceeds with the precipitation of hydrocalumite (Ca$_2$Al(OH)$_7$·3H$_2$O) [1].

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2}$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \tag{3}$$

$$SiO_2 + Ca(OH)_2 + H_2O = CaO \cdot SiO_2 \cdot 2H_2O \tag{4}$$

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{5}$$

$$3Ca(OH)_2 + 2Al(OH)_3 + 3CaSO_4 + 26H_2O$$
$$\rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O \tag{6}$$
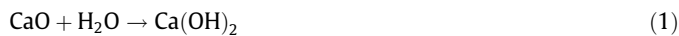
The hydration processes presented above result in the formation of ash stone, which indicates that OSA could be used to backfill OS mines. Maximizing the recovery of OS by backfilling with OSA cement is a promising idea from a waste utilization point of view, however, it also raises concerns about the risks of polluting both surface and groundwater. The ecological risks associated with mineral waste recycling are primarily related to the leaching and distribution of the contaminants [15,17,18].

The current study focuses on the strength development of different types of OSA-based backfilling concretes and observing changes in the mineralogy, structure, and leaching characteristics of these concretes for the dual purpose of optimizing the properties of composite blends and maximizing the share of OSA that could be used for mine backfilling.

2. Materials and methods

OS combustion and mining wastes (OSA-based binder and waste rock-based aggregate) were used as concrete constituents. The PF ash samples (Table 1), including ash from the 1st field of an electrostatic precipitator (PFEF1), cyclone ash (PFCA), ground cyclone ash (gPFCA) and NID (Novel Integrated Desulphurization, Alstom Power [19]) ash from an SO$_2$ removal system as well as CFB ash sample, from the 1st field of an electrostatic precipitator (CFBEF1) were collected from the Estonian Power Plant (Estonia). Grinding of the PFCA was carried out in a multifunctional disintegrator Desi 11 (Desintegraator Tootmise OÜ, Estonia). Previous studies have shown that PF and CFB ashes differ in their chemical and phase composition, structure, and surface characteristics [1,20]. According to Raado et al. [21], coarse PF cyclone ash, which is characterized by a high free CaO content and low specific surface area (Table 1, PFCA), has predominantly non-hydraulic binding properties of an atmospheric binder. Along the ash separation system, the content of free oxides decreases as the content of silicates and aluminates increases, and ash from the electrostatic precipitators (Table 1, PFEF1) have hydraulic binding properties with a pozzolanic effect. The low temperature CFB ashes, which are characterized by a lower content of Ca-silicates and -aluminates and a higher content of quartz and adularia (Table 1, CFBEF1), display a predominantly pozzolanic hydration type [21]. NID ash is a novel type of PF ash that has been characterized and tested for the first time in this study. Carbonated PF ash (Carb PFA) was also included in our studies because OSA can be used as a readily available low-cost Ca-source for CO$_2$ sequestration [22]. We acquired the Carb PFA sample from a continuous accelerated carbonation process that has been described elsewhere by Uibu et al. [22].

OSA binders were mixed together in the proportions provided in Table 2. All concrete mixes contained 50 %-wt OSA-based binder and 50 %-wt pre-dried aggregate (crushed limestone with dimensions 4–16 mm). Concrete constituents were mixed in a laboratory concrete mixer. Water was added until an equal consistence was achieved with a slump of 10–12 cm according to EVS EN 12350-2:2009 [24]. After 48 h of hardening, concrete cubes (10 × 10 × 10 cm) were demoulded and further hardening was carried out for 7, 28 and 91 days at 95 ± 5% RH and 20 ± 2 °C.

The composition, specifications and conformity criteria for the OSA based mineral binders were tested previously using EVS-EN 196 [25], EVS-EN 459-2:2010 [26], and EVS 636:2002 [27] and are described elsewhere [21]. The strength development of OSA based concretes hardened for 7, 28 and 91 days was tested by EVS-EN 12350-2:2009 [24]. The water resistance was tested according to EVS-EN 12390-8 [28] by determining the maximal depth of water penetration under a pressure of 200 kPa. The water penetration tests were carried out with 15 × 15 × 15 cm cubes hardened for 28 days at 95 ± 5% RH and 20 ± 2 °C.

The pore size distribution of cPFEF1, cPFCA and cCFBEF1 was determined by mercury intrusion porosimetry (MIP) using the POREMASTER-60-17 porosimeter (Quantachrome Instruments, USA). The binder stone and the aggregate stone were tested separately.

Whole-rock mineralogical analysis was studied using powder X-ray diffraction (XRD), using a Bruker (Bruker Corporation, USA) 8D diffractometer with Ni-filtered Cu Kα radiation. 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 and unoriented whole-rock preparations was measured using Rietveld based code, Siroquant-3. The proportions of the amorphous (glass like) phases was estimated from its mass-adsorption effect on the patterns with an added spike of a known phase (ZnO). The Scanning Electron Microscopy (SEM) studies of broken surfaces and polished samples were carried out using Zeiss EVO 15 microscope (Carl Zeiss AG, Germany). The areal distribution of different mineral phases and chemical elements were analyzed using an energy-dispersive analyzer (EDS). The SEM was operated at an accelerating voltage of 15–20 kV with a beam current of 30 µA.

A batch leaching test according to European standard EN 12457-2(2002) [23] was carried out to study the leaching of OSA samples. The ash sample (60 g) was leached with deionized water (Milli Q) (liquid to solid ratio 10 L/kg) for 24 h at 20 ± 2 °C. At the end of each extraction, the suspension was filtered through a 0.45 µm filter (HIMFIL, Estonia). Blank tests without an OSA sample but applying the same procedure for deionized water were carried out in parallel. Two replicate samples were used and the test results were averaged (Table 1). A batch leaching test defined by European standard CEN/TS 15862:2012 [29] was carried out to study the leaching characteristics of OSA-based monolithic composites. The sample bodies were contained in deionized water (Milli Q) at a liquid to solid surface area ratio of 12 cm^3/cm^2 ± 2% for 24 h at 20 ± 2 °C. At the end of each extraction, the leachate was filtered through a 0.45 µm filter (HIMFIL, Estonia). The water extracts (leachates) were then used for further chemical analysis. The pH (H$_2$O) and electrical conductivity (EC, µS/cm) were measured using a BENCH PC 510 pH/Conductivity Meter (Eutech Instruments Pte Ltd, Singapore/ Oakland Instruments, Vernon Hills,