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Development of alkali activated cements and concrete mixture design with high volumes of red mud

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HIGHLIGHTS

- The AAC with red mud content 80% and concrete (red mud content 90%) were designed.
- Compressive strength could reach 60 MPa for cements and 70 MPa for concrete.
- Hydration products are calcium silicate hydrates, klinoferrosilite, lawsonite.
- From the radiological point of view materials could be used for road construction.

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ABSTRACT

Dedicated cement compositions were formulated to enable the incorporation of large volume fractions of red mud in alkali activated cements, taking into account the role of the aluminosilicate phase in the processes of hydration and hardening. High volume red mud alkali activated cements were synthesized using a proper combination of red mud, low basic aluminosilicate compounds with a glass phase (blast-furnace slag) and additives selected from high-basic Ca-containing cements with a crystalline structure (Portland cement). Compressive strength of the cements under study is 30–60 MPa (tested in mortar). The microstructure of the hardened cement paste and the role of red mud in the structure formation process were investigated. In addition to the use of red mud in cement, its use as an aggregate in concrete was studied to enable the use of larger quantities in the final concrete. In concrete road bases, the use of red mud can reach even 90% by mass. Since enhanced concentrations of naturally occurring radionuclides can be present in red mud this aspect was investigated to make sure that these materials are safe to use from a radiological point of view.

1. Introduction

The Bayer process is a principal commercial technology to purify bauxite and produce alumina (Al_2O_3). During the Bayer process red mud is produced as a major by-product. It can be a hazardous material owing to its alkalinity but also because of its enhanced levels of natural occurring radionuclides. A typical plant produces up to twice as much red mud as alumina. Today, over 2.7 billion tons is available worldwide [23,34]. Disposal costs of red mud can add up to 5% of alumina production costs and it also introduces risks to the environment. Therefore, a lot of effort is dedicated to find suitable applications for use of the large reserves of red mud that are available worldwide. The use of red mud on a large scale in the production of construction materials can be a commercially viable option. Several studies have investigated the application of red mud as an additive for building materials [36,11,33,39,31,42]. In the preparation of special cements from red mud the added quantity of red mud is usually less than 5% [25,37,33,39]. Alkaline activation allows to considerably increase the quantities of red mud incorporated both in cements and concretes without a decrease of their physico-mechanical characteristics [29,30,17,19,14,44,43,22,5,13,41,20,15,1,18,32]. The limited incorporation levels of red mud can be explained by the fact that such important factors such as the chemical composition of constituent materials, the state of structure and the type of alkaline activator have not

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been optimized. These factors, according to Glukhovsky [10,21] and Krivenko are important with regard to the formation of alkaline and alkaline-alkali earth phases which eventually determine the properties of the resulting cement stone.

An option to use large percentages of red mud is to chemically and thermally convert them to inorganic polymer mortar [16]. The mayor disadvantage of this process is that it is very energy intensive. However, in order to develop an industrially viable option it is crucial to study options for reuse that do not require such an energy intensive pretreatment step.

Red mud has a low hydraulic activity. Any cement composition containing red mud should therefore be modified by activating additives, such as amorphous silica, which do not contain calcium. The main goal of the current research is to optimize the formation process of red mud based alkali activated cements. In order to achieve this goal, it is important to control the alkaline medium (alkalinity) and the presence of oxides, such as CaO, Al_2O_3, SiO_2, Fe_2O_3 and others in the active form. The alkalinity and oxides are required for synthesis of proper hydration products-mineral substances of alkaline aluminosilicate composition. As a rule, these substances act as structure-forming elements not only during the formation of solid rocks in nature, but in ancient concretes as well. Analcime, an alkaline aluminosilicate hydrate composed of Na_2O Al_2O_3 SiO_2 H_2O, is formed in ancient cements and acts as a so-called "eternal" bond. Specific features of ancient cements, distinguishing them from contemporary Portland cements, are the high contents of amphoteric (Al_2O_3 and Fe_2O_3), acid (SiO_2) and alkali metal oxides (Na_2O and K_2O). It is therefore worthwhile to investigate to which extent red muds containing large quantities of amphoteric oxides. Fe_2O_3 and Al_2O_3 (over 60%) could be used as components of the alkali activated cements in long term applications.

More and more attention is payed to the presence of naturally occurring radionuclides in building materials. According to the CPR Construction Products Regulation) the construction works must be designed and built in such a way that emission of dangerous radiation will not be a threat to health of occupants or neighbors. A unified legislation across the Member States of the European Union will come into act in February 2018 i.e. the Euratom Basic Safety Standards EU-BSS, [2]). According to this legislation building materials incorporating naturally occurring radioactive materials NORM), such as red mud, require a radiological screening before approved use as building materials. Red muds can contain enhanced concentrations of naturally occurring radionuclides [38,28,27].

In this study different mixture designs were formulated that enable the incorporation of high percentages of red mud in cement and concrete. To assure safe application of red mud in the different considered mixtures, the radiological properties of the constituents and the resulting construction materials are investigated.

2. Materials and methods

2.1. Constituents

Concrete and cement specimens (d = 50 mm; h = 25 mm) with various incorporation rates of bauxite residue were prepared. The chemical composition of the main constituent materials used in the concrete and cement specimens are given in Table 1.

A Ukrainian red mud of the following mineralogical composition (% by mass): 25–27% hematite, 25–28% goethite, 4.5–6.5% rutile and anatase, 15–17% hydrogarnets, 6–7% sodium aluminosilicate hydrate, 2.5–3.0% calcite was used in the experiments in cements and concretes.

Blast-furnace slag and Ordinary Portland Cement (OPC) were used to introduce aluminosilicate components varying in basicity, expressed by a basicity modulus $\left(M_b = \frac{CaO+MgO}{SiO_2+Al_2O_3}\right)$, and content of glass phase (80% for GGBFS and 5% for OPC measured by XRD analysis) in order to regulate the structure formation processes.

All solid cement constituents excluding alkalis were jointly ground until a fineness of 350–450 m^2/kg (specific surface by Blaine).

Sodium silicate (Ms = 2.8; p = 1300 kg/m^3); soda ash (Na_2CO_3) and sodium metasilicate pentahydrate ($Na_2O \cdot SiO_2 \cdot 5H_2O$) were used as alkaline components.

Local river sand with maximum grain size of 1.2 mm, granite aggregate with fractions 5–10 mm and 5–20 mm, granite screenings (fr. 2.5–5 mm) and red mud with particle sizes varying from 50 to 1000 μm were used as aggregates for concretes.

2.2. High volume red mud alkali activated cements

Different compositions of red mud, ground granulated blast-furnace slag (glassy additive) and OPC (high-basic calcium containing additive) were mixed with soda ash, sodium metasilicate and soluble sodium silicate as alkaline components in order to produce alkali activated cements. An overview of the compositions of the produced alkali activated cements is given in Table 2.

2.3. Red mud containing concretes

Different concentrations of red mud were used as fine aggregate in alkali activated cement concretes. For the concrete mixes given in Table 3, fine aggregate – sand – was substituted for up to 38.6% (by mass) bauxite red mud.

2.4. Methods for physico- mechanical analysis

Physico-mechanical properties of the formulated cements were studied following the Ukrainian national standard DSTU B.V 2.7-181:2009 "Alkaline cements. Specifications". In the preparation of the concretes the Ukrainian national standard DSTU – N B.V.2.7-304:2015 "Manual on the manufacture and use of alkaline cements, concretes and structures" was followed. Specimens were allowed to harden in normal conditions.

Hydration products of the formulated cements were studied using a set of physical- chemical examination techniques, such as X-ray phase diffractometry, differential-thermal analysis (DTA), thermogravimetry and electron microscopy. X-ray phase diffraction analysis was done using diffractometers DRON-3M and

Table 2
Compositions of alkali activated cements containing red mud.

Composition	Red mud, % by mass	ggbs, % by mass	OPC,% by mass
Alkaline component: soda ash (Na_2CO_3)(5% by mass of ggbs + red mud)			
K1	50	50	–
K2	60	30	10
K3	70	30	–
K4	70	20	10
K5	80	15	5
Alkaline component: sodium metasilicate (Na_2SiO_3)(5% by mass of ggbs + red mud)			
K6	50	50	–
K7	70	25	5
Alkaline component: soluble sodium silicate (Ms = 2.8, ρ = 1400 kg/m^3) (soluble sodium silicate/ggbs + red mud = 0.4)			
K8	50	50	–
Alkaline component: soluble sodium silicate (Ms = 2.8, ρ = 1300 kg/m^3) (soluble sodium silicate/ggbs + red mud = 0.4)			
K9	60	30	10
K10	50	50	–

Table 1
Chemical composition of constituent materials.

Cement components	Oxides, % by mass									
	SiO_2	Al_2O_3	MnO	Fe_2O_3	CaO	MgO	TiO_2	R_2O	M_b	Glass content
Red mud	4.8	12.9	–	48.6	10.1	–	5.3	2.5	–	–
Ground granulated blast-furnace slag (ggbs)	37.9	6.85	0.106	–	44.6	5.21	0.35	–	1.0	80
OPC	23.4	5.17	–	4.12	64.13	0.88	–	–	2.27	5